PB-214 771

PILOT SCALE STUDY OF ACID MINE DRAINAGE

Ohio State University Research Foundation

Prepared for:

Environmental Protection Agency

March 1971

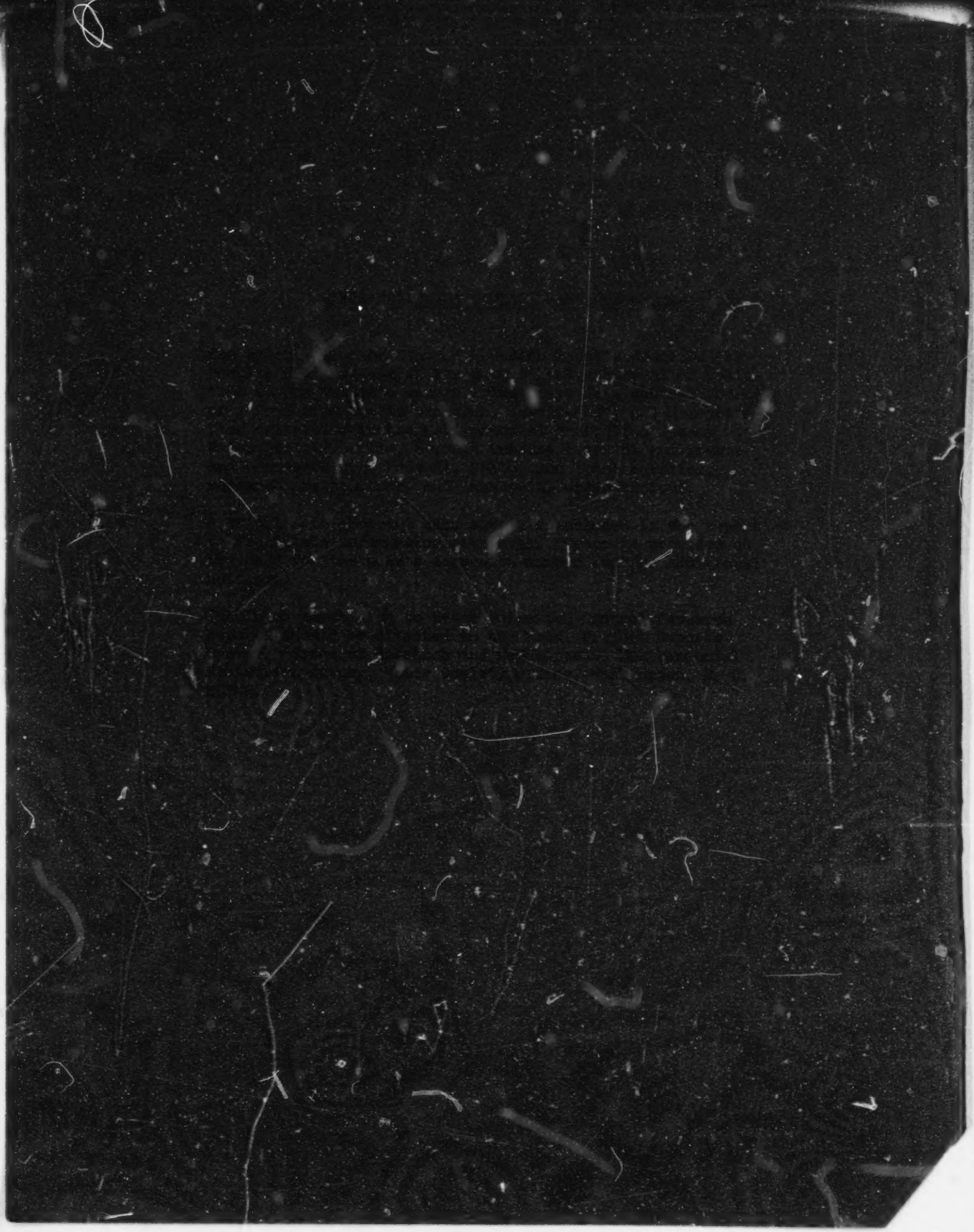
DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 214 771

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151



SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM	W 73-05210

PILOT SCALE STUDY OF ACID MINE DRAINAGE,

14010 EXA

Ohio State University Research Foundation, Columbus

14-12-97

Environmental Protection Agency rept

Water Pollution Control Research Series No. 14010 EXA, March 1971. 84 p. 23 fig, 14 tab., 7 ref., 1 append.

In order to study pyrite oxidation and resulting acid mine drainage, a research facility was developed using a small, long-abandoned drift mine (McDaniels mine) and six 33 inch diameter auger holes drilled in order to have comparable, isolated, experimental "mines" on a pilot scale basis. Experimental data and observations of the effect of oxygen concentration on acid production have shown the location of major reaction zones and indicated that bacterial catalysis of pyrite oxidation is not a significant factor in production of acid mine drainage. When the correspondence between holes has been established, one hole will be used as a reference mine so that fluctuations due to hydrologic variations can be separated from effects of experimentally imposed changes in the other holes. (Smith-Texas)

*Acid mine water, *Coal mines, *Pollution abatement, *Sulfides, *Pyrites, Ohio, Water pollution, Water pollution sources, Environmental control, Research facilities, Industrial wastes

*Auger holes, *McDaniels mine, Underground mines

14010 EXA 03/71
Copy ... from GPO Sup Doc
EPA:WPCRS 14010 ...

05B

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U S DEPARTMENT OF THE INTERIOR
WASHINGTON D C 20240

Richard M. Smith, Jr. | Texas Univ, Austin

Pilot Scale Study of Acid Mine Drainage

by

The Ohio State University
Research Foundation
Columbus, Ohio 43210

for the

WATER QUALITY OFFICE

ENVIRONMENTAL PROTECTION AGENCY

Program # 14010 EXA
Contract 14-12-97
March, 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1.00
Stock Number 5501-0091

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A research facility has been developed to study pyrite oxidation and the resulting acid mine drainage on a pilot scale basis. The test units include a small, long-abandoned drift mine (the McDaniels Mine), and six 33-inch diameter auger holes, drilled for the express purpose of furnishing comparable, isolated, experimental units. McDaniels is a single room of approximately 600 square feet and an average height of three feet. Four of the auger holes are approximately 200 feet deep, while the other two are approximately 100 foot each. All units are in the Middle Kittanning seam and are located within a radius of 200 yards. They can be opened or sealed at will and are equipped and instrumented to allow the observation of the effects of imposed mine atmospheres on the production of acid mine drainage.

The effect of oxygen concentration on acid production has been studies in the McDaniels mine. The response time of the mine to imposed mine atmospheres of varying oxygen concentrations, mine drainage data, and information derived from bore holes through the overburden around the mine, provide the basis for describing sites of pyrite oxidation and the significance of bacterial catalysis on oxidation rate. Results to date indicate that the major reaction sites are located above the ground water table where gas, rather than liquid, is the continuous phase. There is no indication of significant bacterial catalysis of pyrite oxidation.

The six auger holes were drilled in order to provide duplicate experimental units. By using one or more of the holes as a reference mine, the fluctuations due to hydrologic variations can be separated from changes brought about by an imposed change in environmental conditions, and a more accurate evaluation of the effect of the environment on mine drainage can be made. The units also provide experimental flexibility and enhance the progress of the experimental program which is restricted to one experiment per year per unit by annual ground water fluctuations and by the slow response time of underground pyritic systems to imposed environmental changes.

This report was submitted in fulfillment of Contract No. 14-12-97 (Program #14010 EXA) under the sponsorship of the Water Quality Office of EDA.

Key Words: Mine drainage,* pyrite,* sulfides,* Ohio,* auger holes,* underground mines,* coal,* pollution abatement, industrial wastes

TABLE OF CONTENTS

	Page
CONCLUSIONS	1
RECOMMENDATIONS	3
INTRODUCTION	5
RESEARCH FACILITIES	9
EXPERIMENTAL PROGRAM	27
EXPERIMENTAL RESULTS	33
DISCUSSION OF RESULTS	47
ACKNOWLEDGMENTS	63
REFERENCES, LIST OF PUBLICATIONS	65
GLOSSARY	67
APPENDIX I -- DISCHARGE DATA	6.
ABSTRACT CARDS	

TABLES

Table		Page
I	Sulfur Analysis From McDaniels Test Mine	11
II	McDaniels Test Mine Operating Conditions	27
III	Average Monthly Acid and Sulfate Loads For McDaniels Mine	34
IV	Average Monthly Acid and Sulfate Loads For Auger Holes	35
V	Air "Permeability" Measurements	45
VI	Experimental "Weeping" Rate	50
VII	McDaniels Mine Discharge Data	69
VIII	Auger Hole No. 1 Discharge Data	77
IX	Auger Hole No. 2A Discharge Data	79
X	Auger Hole No. 2B Discharge Data	80
XI	Auger Hole No. 3 Discharge Data	81
XII	Auger Hole No. 4 Discharge Data	82
XIII	Auger Hole No. 5 Discharge Data	83
XIV	Auger Hole No. 6 Discharge Data	84

FIGURES

Figure		Page
1	Planimetric Map of McDaniels Mine and Observation Wells	10
2	Outcrop Map	14
3	Contour Plat - Floor of McDaniels Mine	15
4	Contour Plat - Roof of McDaniels Mine	16
5	Plan View - Auger Hole Placement	18
6	Plan and Elevation - Views of Hole No. 1	19
7	Plan and Elevation - Views of Hole No. 2A	20
8	Plan and Elevation - Views of Hole No. 2B	21
9	Plan and Elevation - Views of Hole No. 3	22
10	Plan and Elevation - Views of Hole No. 4	23
11	Plan and Elevation - Views of Hole No. 5	24
12	Plan and Elevation - Views of Hole No. 6	25
13	Oxygen Concentration McDaniels Mine	28
14	Monthly Average Acid and Sulfate Loads for McDaniels Mine	36
15	Monthly Average Acid and Sulfate Loads for Auger Hole No. 1	37
16	Monthly Average Acid and Sulfate Loads for Auger Hole No. 2A	38
17	Monthly Average Acid and Sulfate Loads for Auger Hole No. 2B	39
18	Monthly Average Acid and Sulfate Loads for Auger Hole No. 3	40
19	Monthly Average Acid and Sulfate Loads for Auger Hole No. 4	41

FIGURES (continued)

Figure		Page
20	Monthly Average Acid and Sulfate Loads for Auger Hole No. 5	42
21	Monthly Average Acid and Sulfate Loads for Auger Hole No. 6	43
22	Depth of Water in Well No. 6 vs. Mine Drainage Flow Rate	44
23	Model of Underground Pyritic System	52

CONCLUSIONS

1. Field data from underground mines indicate that the major sites of pyrite oxidation lie above the ground water table, in regions where gas rather than liquid is the continuous phase. Oxygen transport to the pyrite oxidation site occurs by both convection and diffusion through the gas phase.

2. Since pyrite oxidation sites are located above the ground water table, the transport of oxidation products away from the pyrite is a slow process. With product transport being limited to either 1) molecular diffusion along water films, 2) seepage ("weeping") induced by the hygroscopic nature of the oxidation products, 3) occasional downward percolation of precipitation, and 4) flushing of restricted regions by annual changes in ground water table elevations, the retention time of oxidation products in the mine varies widely with the specific location of the pyrite being oxidized. In the case of the small abandoned drift mine studies in this work, one hydrologic cycle does not remove all oxidation products from the system, and it is unlikely that complete removal is obtained even after three or four cycles.

2. There are direct indications that a significant portion of the water flowing into the mined-out volume from the surrounding ground water flow regions is essentially free of acid, i.e., most of the drainage has never come in direct contact with active pyrite oxidation sites.

4. There is no evidence of significant bacterial catalysis of pyrite oxidation in the mines under investigation. While autotrophic iron-oxidizing bacteria are active in the drainage after it has left the pyrite oxidation sites and has been diluted with ground water, bacteria are not present in sufficient numbers at the oxidation sites to significantly affect the rate of pyrite oxidation. The predominant mode of pyrite oxidation is the direct oxidation of pyrite by oxygen (oxygenation).

5. The six recently drilled auger holes were designed to have a high degree of similarity, allowing one to be used as a control and the remaining five to be available for controlled experimentation. However, the six units differ widely in regard to both drainage quality and quantity. This is due to differences in the amount of ground water flow intercepted by the various holes.

6. The auger holes, although two years old, have not yet reached a stable acid production rate because of the long period of time required to reach a steady-state relation between pyrite oxidation rate and product removal rate. It now appears that at least four years will be

required for the product removal rate to reach 90 percent of the ultimate steady-state value.

7. Analysis of underground pyritic systems is hampered by lack of detailed information on the physical, chemical, and microbiological conditions at reaction sites. There is obviously a wide range of conditions in respect to oxygen concentration, water flow, and dispersal rate of oxidation products, depending on the location of a reaction relative to the strata and to distance from the working face. However, it is experimentally impossible to directly measure these conditions. Therefore, interpreting the effects of imposed environmental changes on acid production rates in accordance with a realistic model of an underground pyritic system appears to offer the best approach to quantitatively evaluating such a system. Since accurate data on the effect of imposed changes must be available for this interpretation, an experimental facility of the type described in this report is required to obtain sufficiently reliable information.

RECOMMENDATIONS

Many of the difficulties in interpreting mine drainage field data are related to the slow time response of natural systems to imposed environmental changes, and the erratic output due to hydrologic variations. These factors make it impossible to draw reliable conclusions based on data from a single mine's discharge data over a one or two-year period.

Precise, reliable data are required to determine the kinetics of mine drainage discharge. Only one type of experimental facility, the multiple mine complex, is capable of providing data of the type needed for interpretation of mine drainage kinetics. By using one of the multiple mines as a reference or base control, the effect of hydrologic variations can be determined and separated from changes caused by planned alterations in environment in the other mines.

We, therefore, recommend that work at the multiple mine complex (the McDaniels research facility) be continued with immediate studies made as outlined below:

1. McDaniels mine be maintained under a nitrogen atmosphere for at least two more years in order to more accurately evaluate response time (and, therefore, information on the relative importance of the various removal mechanisms) and to reduce inventory of stored oxidation products so that the effect of a step change in oxygen concentration can be more accurately evaluated.

2. A tracer gas should be added to Auger Hole No. 4 and the drainage asymmetry evaluated by observing the concentration of the tracer dissolved in the discharge from Holes 3 and 5-6. (Holes 5 and 6 will be treated as one experimental unit for reasons discussed in Section VII). If essentially the same quantity of the tracer is removed in the discharge from Hole 3 and in Holes 5-6, the effect of drainage asymmetry, which must exist due to the natural dip of strata in the area, is negligible in regard to drainage of reactive volumes of individual auger holes.

3. Since the auger holes have not yet reached "steady-state" conditions, we recommend that three of the holes be used as controls, and three be used for experimentation.

4. The following environmental conditions are recommended for study:

   a. Sealing, with maintenance of a slight partial pressure of ethylene oxide in an otherwise

normal atmosphere. This will eliminate bacterial catalysis of pyrite oxidation if it is present, and will allow a more direct determination of the significance of bacterial activity than is presently possible.

b. Sealing, with maintenance of a carbon dioxide atmosphere. This could be coupled with the application of carbon dioxide with an internal burner, operated in response to barometric pressure changes.

c. Sealing, with cyclic pressurization to amplify the effect of breathing. By positive control of the breathing component of the oxygen transport process, and observation of the resulting effect on acid production rate, it may be possible to separate breathing and diffusional transport, and to obtain a more quantitative description of both processes.

5. We recommend that one of the reference auger holes be used to see if it can be operated as a large respirometer. If successful, a direct determination of oxygen consumption could be made. This would be a "breakthrough" in the study of natural systems, both in terms of time required to evaluate experimental programs and in the accumulation of data to assist in describing the kinetics of mine drainage production. In order to operate a hole as a respirometer, a method to eliminate the effects of atmospheric pressure changes ("breathing") on gas phase transport to the mine must be provided. We hope to accomplish this by use of inflatable bags to change the volume of the mine in response to atmospheric pressure change so that there will be no flow of gas in or out of the mine.

INTRODUCTION

The phenomenon of acid drainage formation and discharge from underground mines has long been the subject of intensive study. These investigations have been either 1) laboratory scale investigations in which the reactive material was removed from its natural environment, or 2) demonstration type studies in which the effect of proposed abatement measures have been observed on full-scale mining operations. While yielding valuable information, it has not been possible to extrapolate laboratory findings to the field, nor to interpret demonstration efforts in terms of basic mechanisms. The use of available laboratory and demonstration project data and the development of engineering procedures for the abatement of acid mine drainage at the source depend on the identification of the rate controlling mechanisms in the mine environment. Thus it is necessary to determine the nature of the reaction, the location of the reaction sites, the conditions prevailing at the reaction sites which determine the nature of the reaction, and the mechanisms by which reactants and products are transferred to and from the sites.

The specific objectives of this project were to:

1. Determine the effect of oxygen concentration in the mine on the rate of acid discharge (see page 55).

2. Determine the effect of microbiological factors on the rate of acid discharge from the mine (see page 57).

3. Determine the location of reaction sites in relation to the exposed coal surface and the characterization of conditions predominating at the reaction site (see page 48).

4. Determine the mechanisms of reactant and product transport to and from the reaction sites by "time response" studies (see page 49).

The proven inability of laboratory and demonstration scale studies to provide concrete answers to the above objectives points to the conclusion that such answers will be obtained only by using pilot scale facilities, situated in representative coal seams, and intermediate in scale between laboratory studies and demonstration projects. Such natural environment facilities should be viewed as pilot-scale reactors in which the kinetics of the reaction taking place within the reactor can be varied beyond the normal operational range in order to develop fundamental information on reaction kinetics, a situation not possible in demonstration projects. Previous work with this type of system is limited to studies by the Ohio State University at the McDaniels Test

Mine, located in Vinton County, Ohio. Active research at this site has been in progress since 1964 (7). Experience with this facility has indicated the applicability of the pilot scale approach to accomplishment of the objectives outlined above, and a tentative conceptual model of the physical characteristics of the reaction system has been derived from the preliminary data (4). Equally important, techniques and limitations pertinent to the use of this type of facility have been defined. The major limitation is the severe restriction on the rate at which data can be collected from a single unit. The natural ground water hydrologic cycle results in increasing drainage flows during four to five months of the year, the peak flows usually being attained in May. During periods of increasing flow, mine drainage acidities reflect both pyrite oxidation rate and the rate of release of previously stored oxidation products by the increased flows.

On the other hand, during periods of dropping ground water levels and decreasing flows, the slow seepage of highly acid solutions downward to flowing ground water channels will not keep pace with the changing ground water flow patterns. This will result in a lag in product removal, and the accumulation of oxidation products in the system. Thus, acidity appearing in mine drainage is not in equilibrium with the rate of pyrite oxidation. Over a long period of time a "steady state" condition will be reached in which the amount of oxidation product removal will be equal to amount of product formed over the same time period.

The slow transport of acid products to the mine effluent will cause problems in the interpretation of mine effluent data following the alteration of environmental conditions within the mine. There will be a response time delay before the effluent will begin to reflect the change, and the approach toward a new "steady-state" value may be quite slow.

With regard to data interpretation, experience with the McDaniels Mine has shown that "base-line" information is erratic; that is, it is a function of the hydrologic characteristics of the system, particularly as reflected in the ground water influx rate to the mine. These rates are subject to major fluctuations. The use of a reference or control mine to smooth out the effect of base line fluctuations in acid production with varying flows may overcome this problem. A reference mine implies the necessity of similar multiple units.

Due to annual cyclic fluctuations of ground water flow, discharge data can only be compared with regard to the annual pattern. For example, acid loads at the time of maximum ground water flow in the Spring, and minimum flow in the Fall are two sets of reference points frequently used for comparison of discharge data. Note that the comparison is made between points essentially one year apart. With comparative data restricted to a one year interval, and with slow response to impressed environmental changes, one alteration in test conditions per year is the most that can be carried out with a single unit. These restrictions, together with the difficulties in obtaining base line data, point to the

desirability of having multiple pilot-scale facilities, thereby allowing the objectives of the project to be attained more accurately and quickly.

The decision was made to construct the multiple unit pilot scale facility. Alternative approaches to the construction of such a facility were examined in detail. The most satisfactory solution from both an operational and economical point of view was found to be a series of auger holes drilled into an exposed high wall located in the same hollow as the McDaniels Test Mine.

Specific advantages of this arrangement are:

1. The auger holes are in the same coal seam as the McDaniels Test Mine and only a matter of several hundred feet away, and thus the variability of coal seam and overburden characteristics are held to a minimum. The duplication of geologic and geometric features is an extremely important feature of the multiple-unit concept, impossible to achieve by the use of selected abandoned mines.

2. By using an auger rather than conventional mining procedures, a much higher ratio of reaction sites to mined volume is achieved, and it is possible to drive relatively far back into the coal seam without creating an excessively large volume. A small volume is desirable because, in controlled atmosphere composition experiments, the volume will be a determining factor, along with leakage rate, in the amount of gas and time required to reach the desired composition. Conventional mining procedures would result in a mine of not less than twelve foot width, having a high volume to surface area ratio. From this standpoint, abandoned mines would also be less desirable.

3. The nature of the auger holes makes them much more easily and economically sealed than units mined by conventional methods. In addition, seals of the type applicable to augered holes can be relocated at will within the hole with a minimal expenditure of time and material.

4. The location of the multiple units in proximity to the McDaniel' mine makes available existing electrical service and on-site laboratory space, and facilitates efficient operation and maintenance of the research program.

RESEARCH FACILITIES

McDaniels Mine

Major renovation and instrumentation of the McDaniels mine was completed under Project No. A-001-OHIO, Office of Water Resources Research, U. S. Department of Interior (7). A brief description of this phase of the project is given below.

Preparation of Site

Prior to May 8, 1965, the mine had been flooded to a depth of approximately three feet above the outlet valve in the mine seal (which was constructed in 1957). On May 8, the valve was opened and the mine drained. Before draining the mine, samples were taken of the atmosphere in the mine above the impounded water. During the draining operation, samples were taken of the drainage which was concurrently treated with slaked lime to decrease deterioration of water quality in the stream below the mine. On May 18, the manhole cover in the seal was removed, and the interior of the mine was examined. The mine was found to be structurally sound, and plans were made for an accurate planimetric survey of the mine interior. Reference spads were set in the mine roof, and a reference line extended through the seal into the open area in front of the mine. The planimetric survey was finished on June 3, and reference points were placed on the hillside above the mine. The outline of the mine was traced on the hillside, which allowed the selection of sites for five of six observation wells. The location of the sixth well was determined at the time of the drilling of the wells. A planimetric map of the mine and the prepared observation wells is given in Figure 1.

After the locations of the wells were determined, the requisite depths of the wells were estimated, and it was found that the budget would allow the holes to be cored, thereby yielding the maximum possible amount of detailed information on the sub-surface geology of the area surrounding the mine. The drilling was completed during the first week in August.

Boring log plus soil sample and rock cores indicate that the 24' to 35' of sandstone overlaying the coal seam is the primary aquifer supplying the McDaniels Mine. The observation wells provide a means of establishing the approximate contour of the ground water table. Only one well (No. 6) shows a significant head of water above the coal.

Samples of the coal and of the shale and clay partings at three points in the mine were collected and examined for "forms of sulfur." Results of analyses are presented in Table I.

Preceding page blank

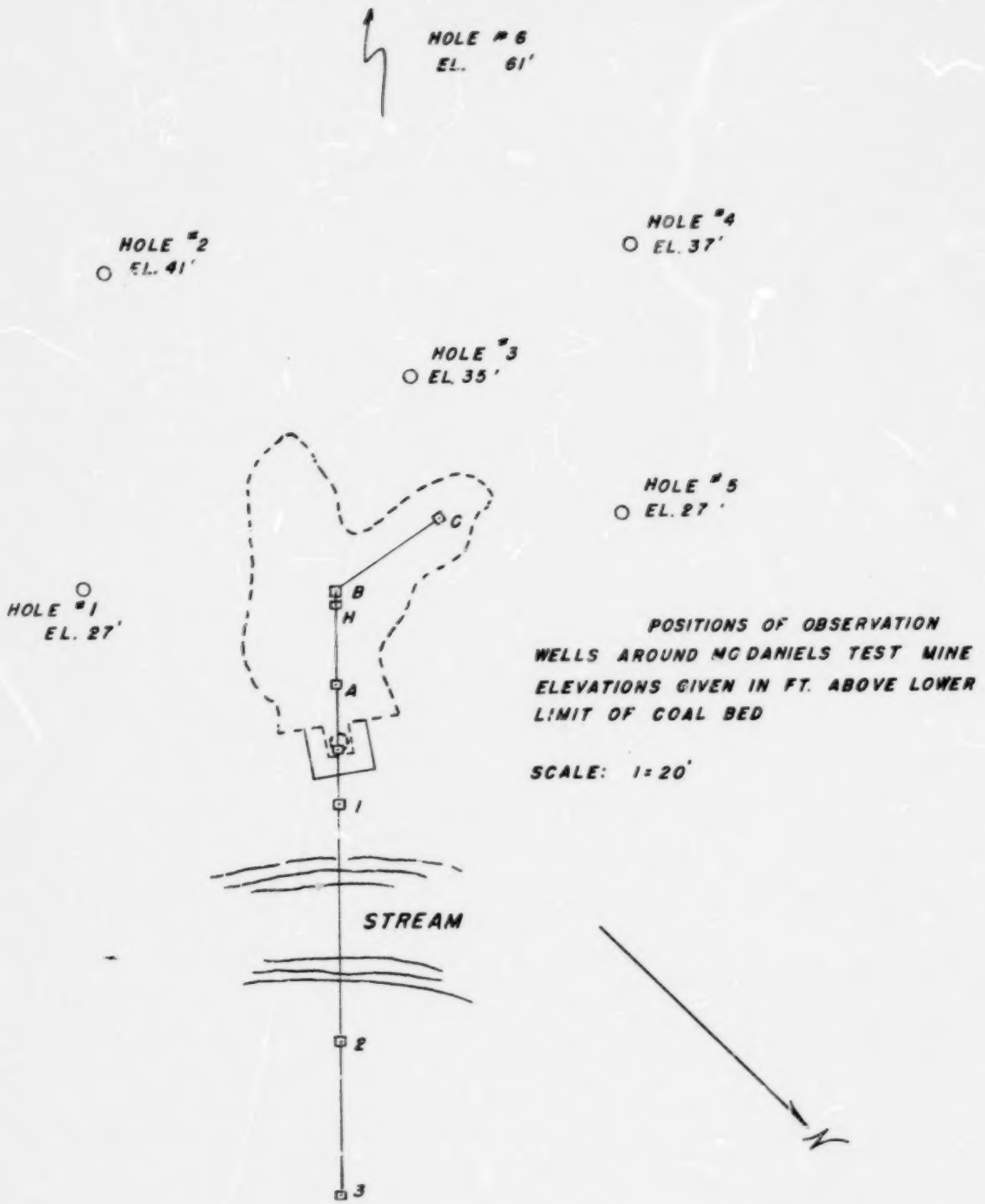


Fig. 1 - Planimetric Map of McDaniels Mine and Observation Wells

Table I. Sulfur Analysis from McDaniels Test Mine

Drill (Face) Samples:

Sample Location No. 1 (Ten feet to left of entrance)

Level	Depth	Percent of Sulfur*			
		Total	Sulfate	Pyritic	Organic
Overburden	0-3 "	7.74	0.97	6.43	0.34
Top 1/3	0-3""	2.02	0.21	1.10	0.71
Top 1/3	3-12"	1.81	0.19	0.91	0.71
Shale parting	0-3 "	4.26	0.86	3.03	0.37
Shale parting	3-12"	10.74	0.93	9.51	0.30
Middle 1/3	0-3 "	1.94	0.20	0.91	0.83
Middle 1/3	3-12"	2.78	0.29	1.61	0.88
Lower 1/3	0-3 "	3.49	0.60	2.37	0.52
Lower 1/3	3-12"	4.05	0.79	2.68	0.59
Sample Location No. 2 (Left-center, back wall)					
Top 1/3	0-3""	2.45	0.28	1.49	0.68
Middle 1/3	0-3 "	2.82	0.28	1.86	0.68
Shale Parting	0-3 "	2.28	0.08	1.87	0.33
Lower 1/3	0-3 "	3.52	0.49	2.36	0.67
Sample Location No. 3 (28 feet from entrance along right wall)					
Top 1/3	0-3 "	4.35	0.51	3.12	0.72
Top 1/3	3-12"	3.26	0.41	2.18	0.67
Middle 1/3	0-3 "	3.16	0.46	2.05	0.65
Lower 1/3	0-3 "	2.55	0.31	1.59	0.65

Core Samples

Core No. 1

Description	Level	Percent of Sulfur			
		Total	Sulfate	Pyritic	Organic
Top-above Shale	26.6'	9.69	0.66	8.58	9.69
Shale parting	26.8'	5.18	1.15	4.03	0.00
Middle coal	27-29.5'	4.20	0.40	3.25	0.55
Bottom coal	29.5-30.2'	3.53	0.49	2.46	0.58

Table I. (continued)

Core No. 2		Percent of Sulfur*			
Description	Level	Total	Sulfate	Pyritic	Organic
Top coal layer	(approx. 6")	5.98	0.90	4.41	0.67
Middle coal		5.10	0.40	4.07	0.63
Shale parting	(6" from bottom)	0.40	0.03	0.12	0.25
Bottom coal	(last 6")	3.07	0.31	2.20	0.56
Core No. 3					
Top 4" coal		8.87	0.64	7.83	0.40
Shale parting	4" from top	11.30	1.14	9.98	0.18
Middle layer	5.05				
Shale parting	(4" thick,6" from bottom)	3.04			
Bottom coal		4.18			
Core No. 4					
Top 4"		6.63			
Middle coal		4.40			
Shale parting	(6" from bottom)	1.06			
Bottom coal		2.80			
Core No. 5					
Very top		16.96			
Top shale	(24.4-27')	0.72			
Middle coal	(24.4-27')	5.05			
Shale parting	(27.5')	0.61			
Bottom coal	(27.5-28.0')	2.62			
Core No. 6					
Top coal	(first 4")	6.11			
Shale parting	(4" from top)	1.04			
Middle coal		4.81			
Shale parting	(6" from bottom)	0.26			
Bottom coal	(lower 6")	2.98			

*Moisture-Free Sulfur

In addition to planimetric mapping of the mine's interior (Figures 3 and 4), elevation bench marks have been established in the Big Four Hollow in which the mine is located, and out-crop elevations determined down to State Highway 278 (Figure 2). The dip of strata and topography in the general area of the mine have thus been established.

During the latter stages of active mining, gob from the operation was piled against the coal faces not being worked instead of being carted from the mine. In order to have a good measure of the coal seam exposed and to gain a better-defined environment within the mine, it was decided to remove this refuse. The job was completed early in September, 1965.

Construction of an adit was completed soon after the gob was removed. The adit replaced the frame structure which originally covered the mine seal and consisted of a small cement block building enclosing the seal, with an adjoining 8' by 8' room equipped for use as an analytical laboratory and housing for recording instruments. A single phase 220 VAC power line was contracted and run back to the adit to provide a sufficient source of electrical power for the multiple mine complex.

The original seal was constructed of hollow concrete block and painted with "Thoroseal". When preparing the front wall of the box entry (Figure 3) for mounting the sampling line panel, it was discovered that the second and third tier of block were disintegrating from the inside out due to the action of acid water which had leaked into the hollow core of these blocks. Where the block core had been grouted, no evidence of attack was apparent. Damaged portions of the box entry were replaced with solid block, and the entire surface coated with a bituminous sealer.

The main wall of the seal was in excellent condition and required little repair.

A new pressure type manhole cover was purchased and installed and a stainless steel panel for mounting sampling lines was mounted in the front wall of the box entry.

The "permeability" of the mine to air was determined by raising the pressure in the mine to approximately 20 cm. of water and observing the rate of pressure decline. From these data it was possible to calculate the amount of gas required to maintain a given pressure differential between mine and atmosphere.

Assuming no net change in atmospheric pressure over a week's period, it was found that 600 cu.ft. of air per week would be lost if a differential pressure of 1.0 mm. of water was maintained. This is equivalent to slightly less than 3 "K" cylinders of oxygen or nitrogen, which may be readily transported and installed once a week.

A rain gauge and water level recorder for Well No. 6 were installed at the site.

Figure 2
Outcrop map showing measured elevations at bottom of coal, and elevations from mine maps

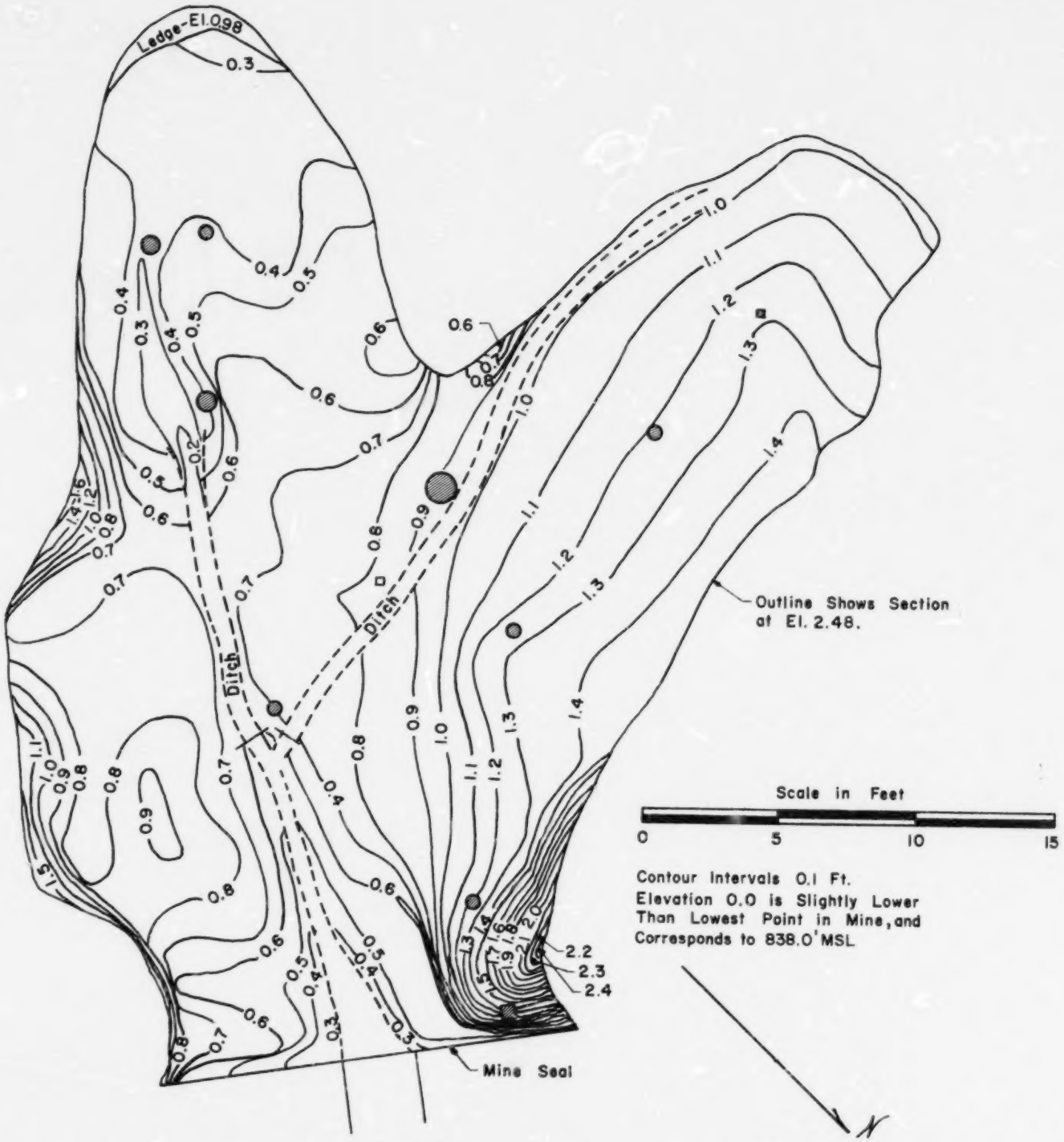


Fig. 3 - Contour Plat - Floor of McDaniels Mine

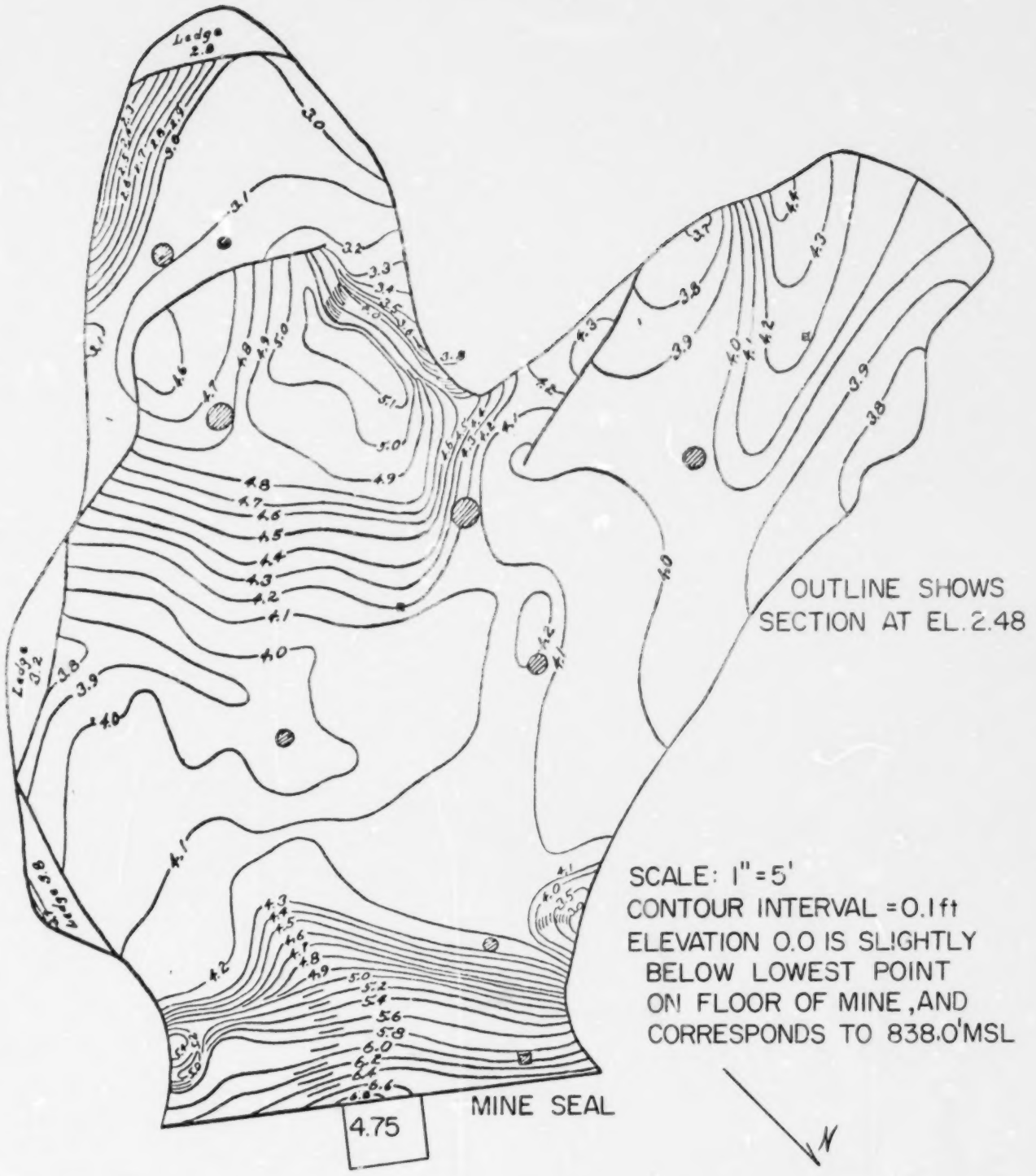


Fig. 4 - Contour Plot - Roof of McDaniels Mine

Auger Holes

Figure 5 shows a plan view of the auger hole placement. All seven holes were drilled in an old strip mine high wall, on the north side of the valley containing the McDaniels Mine. The McDaniels Mine, not shown in the figure, is dug into the coal outcrop on the south side of the valley, and lies approximately 140 feet south of Hole No. 1. A small intermittent stream entering the valley between Holes 2-B and Hole 3 makes the highwall discontinuous at this point, and effectively isolates Hole 2-B from Hole 3.

Figures 6 through 12 show the plan and elevation views of Holes 1 through 6, respectively. The diameter of each hole is approximately 33 inches, and while it was intended that the holes stay in the coal for their entire length, it was not possible to accomplish this, due to the tendency of the auger to drop into the clay. The dip of the coal strata to the southeast is evident in comparing elevations from hole to hole.

The sequence of material adjacent to the Middle Kittanning (No. 6) coal bed is relatively consistent. The coal is underlain by blue clay, and overlain by sandstone. A lightly variable shale parting exists near the top of the coal seam, and a consistent shale parting of 1/2 to 1 inch thickness is present in the coal about 6 inches above the under clay.

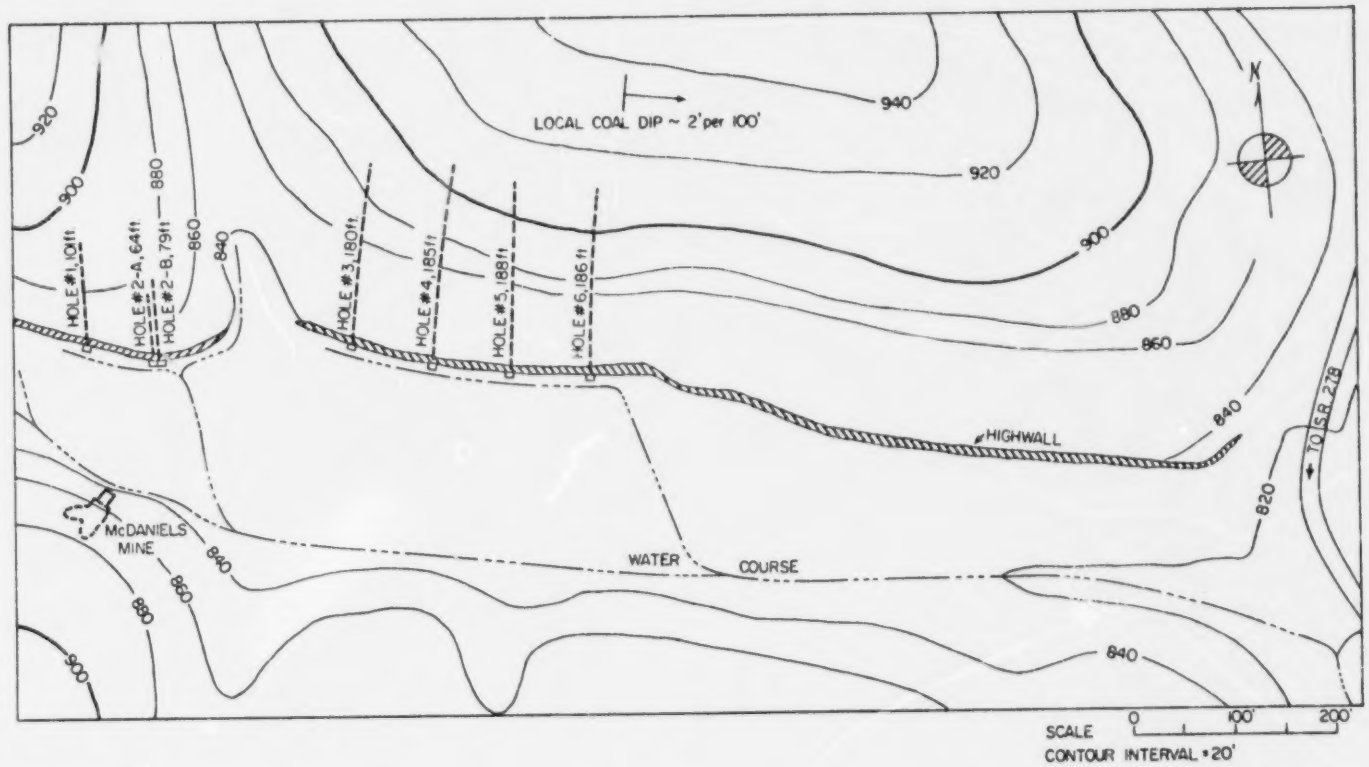


Fig. 5 - Plan View - Auger Hole Placement

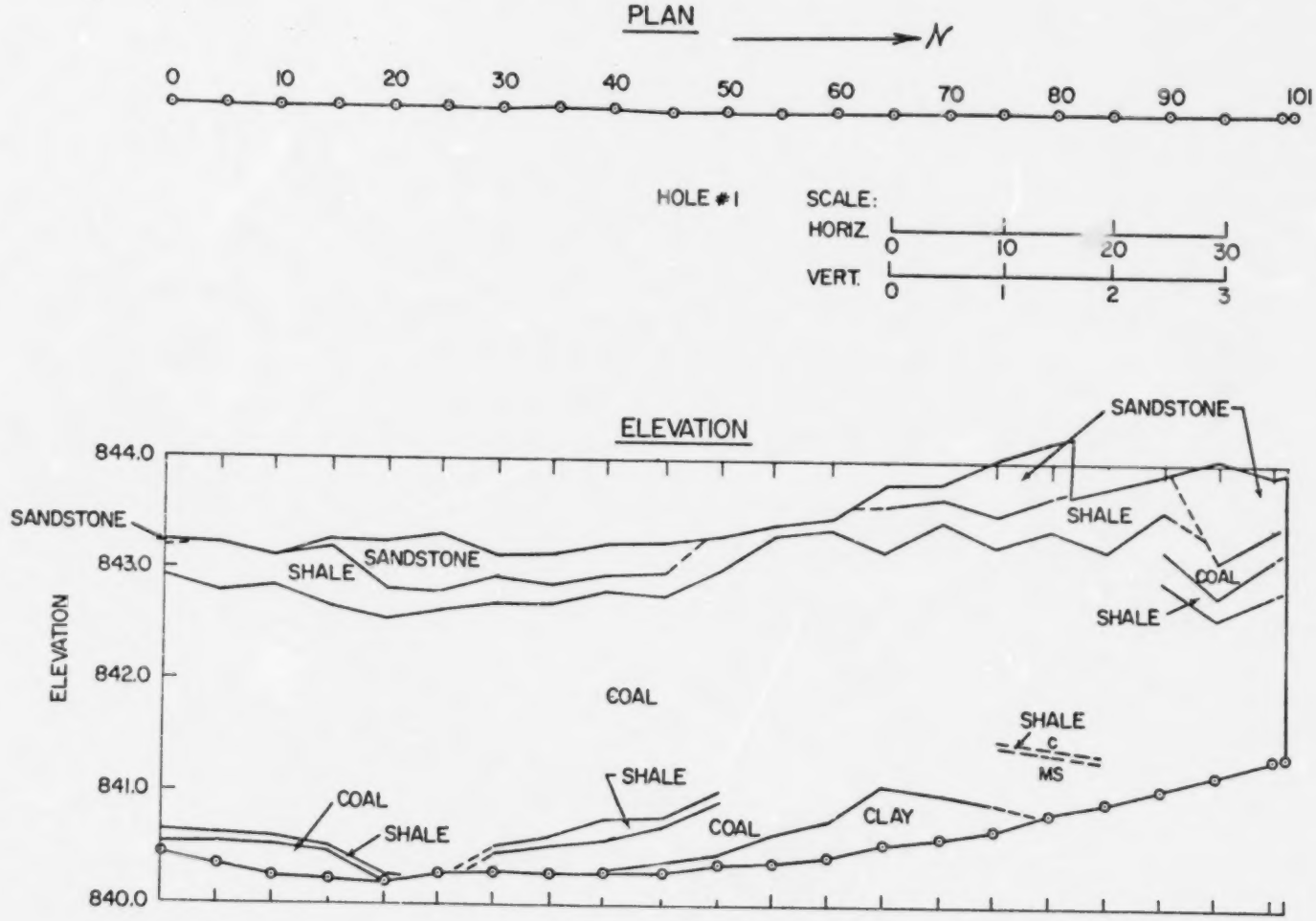


Fig. 6 - Plan and Elevation - Views of Hole No. 1

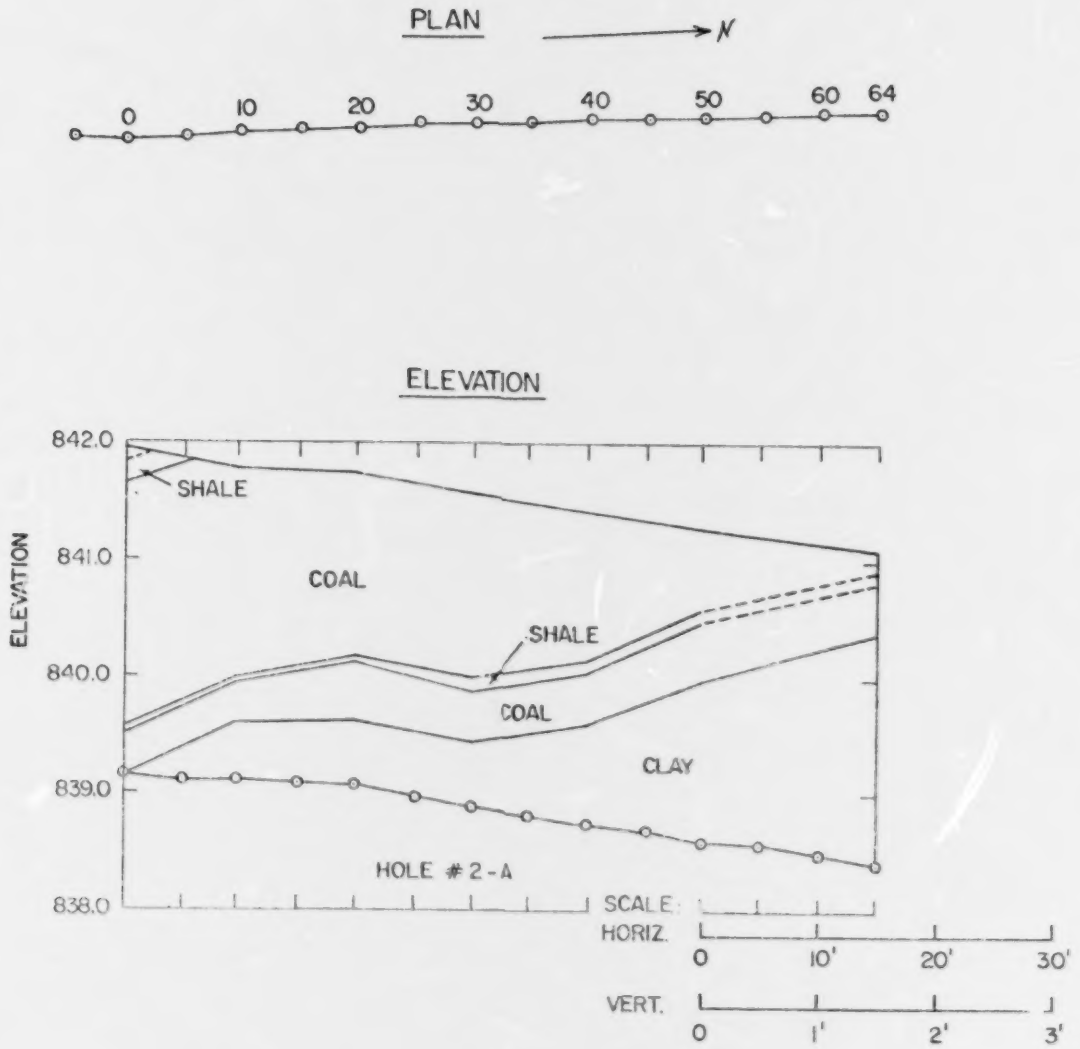


Fig. 7 - Plan and Elevation - Views of Hole No. 2A

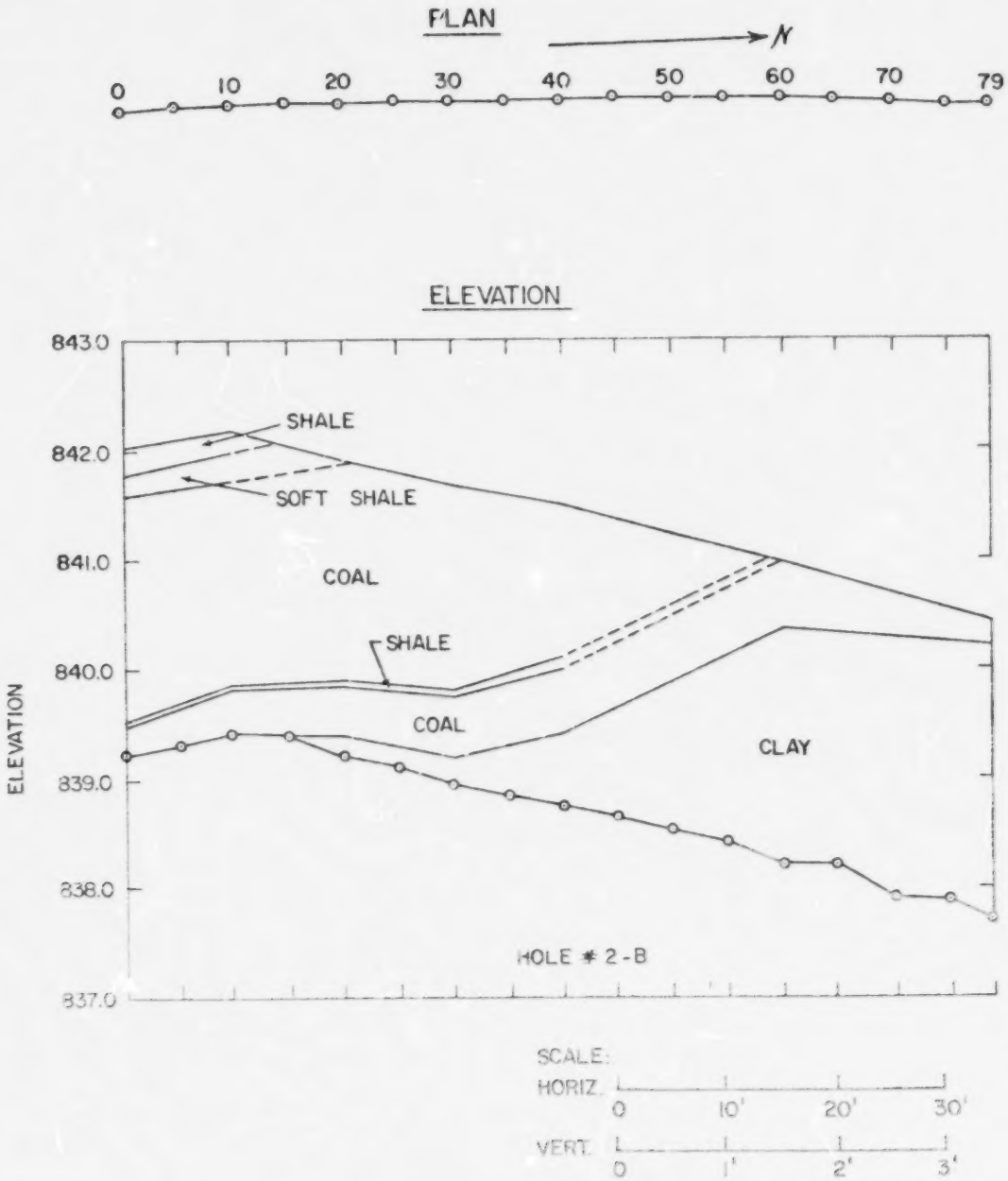


Fig. 8 - Plan and Elevation - Views of Hole No. 2B

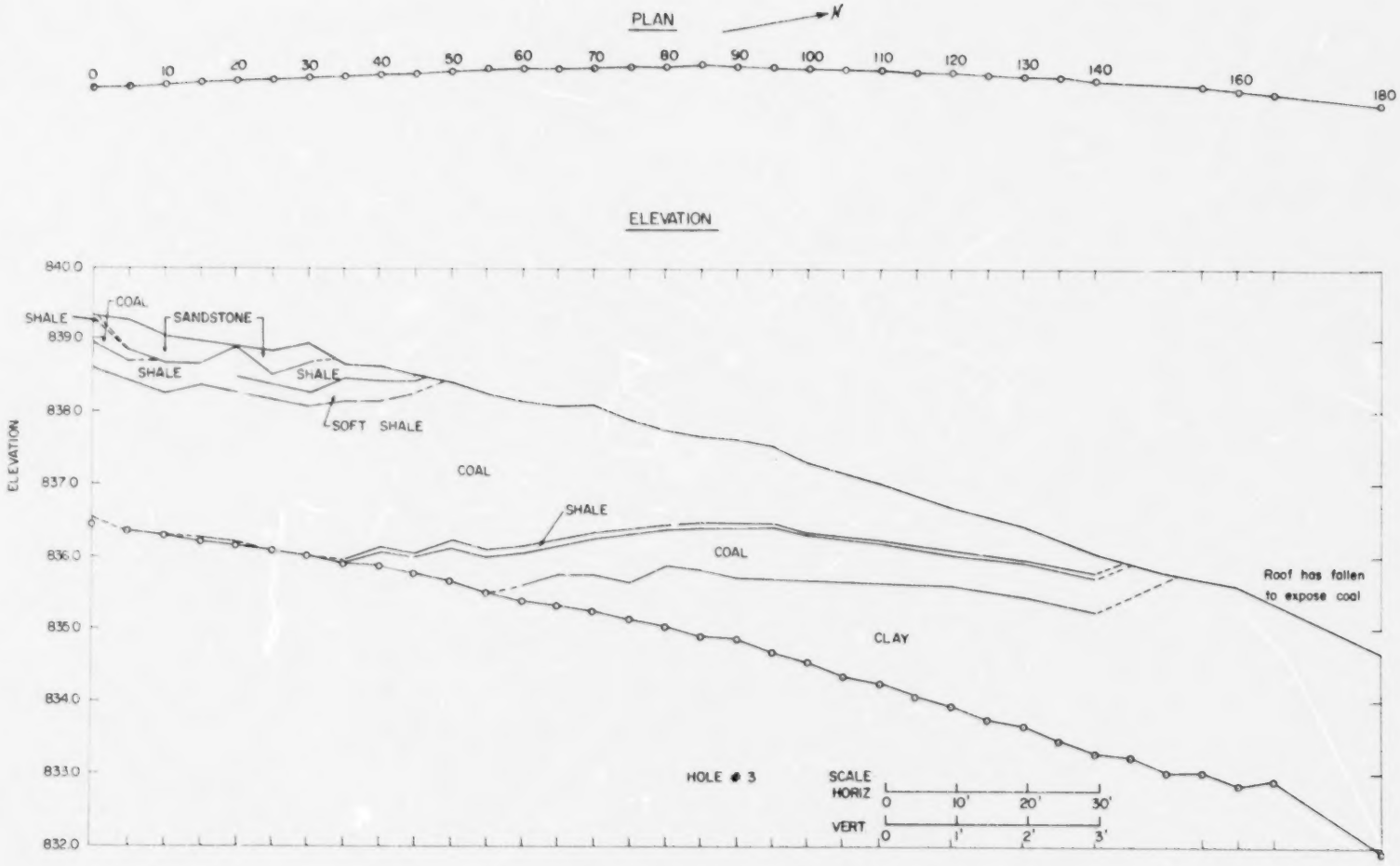


Fig. 9 - Plan and Elevation - Views of Hole No. 3

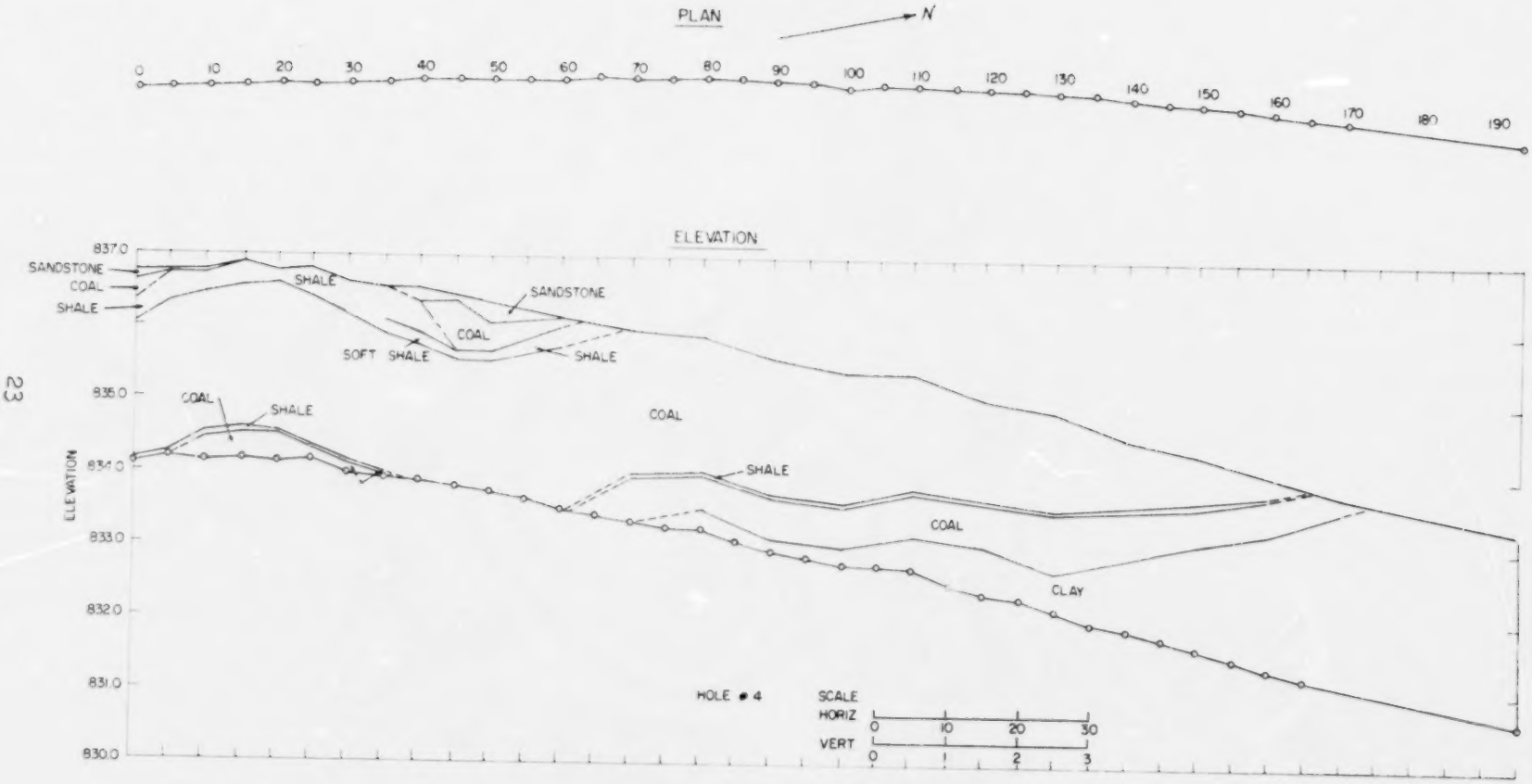


Fig. 10 - Plan and Elevation - Views of Hole No. 4

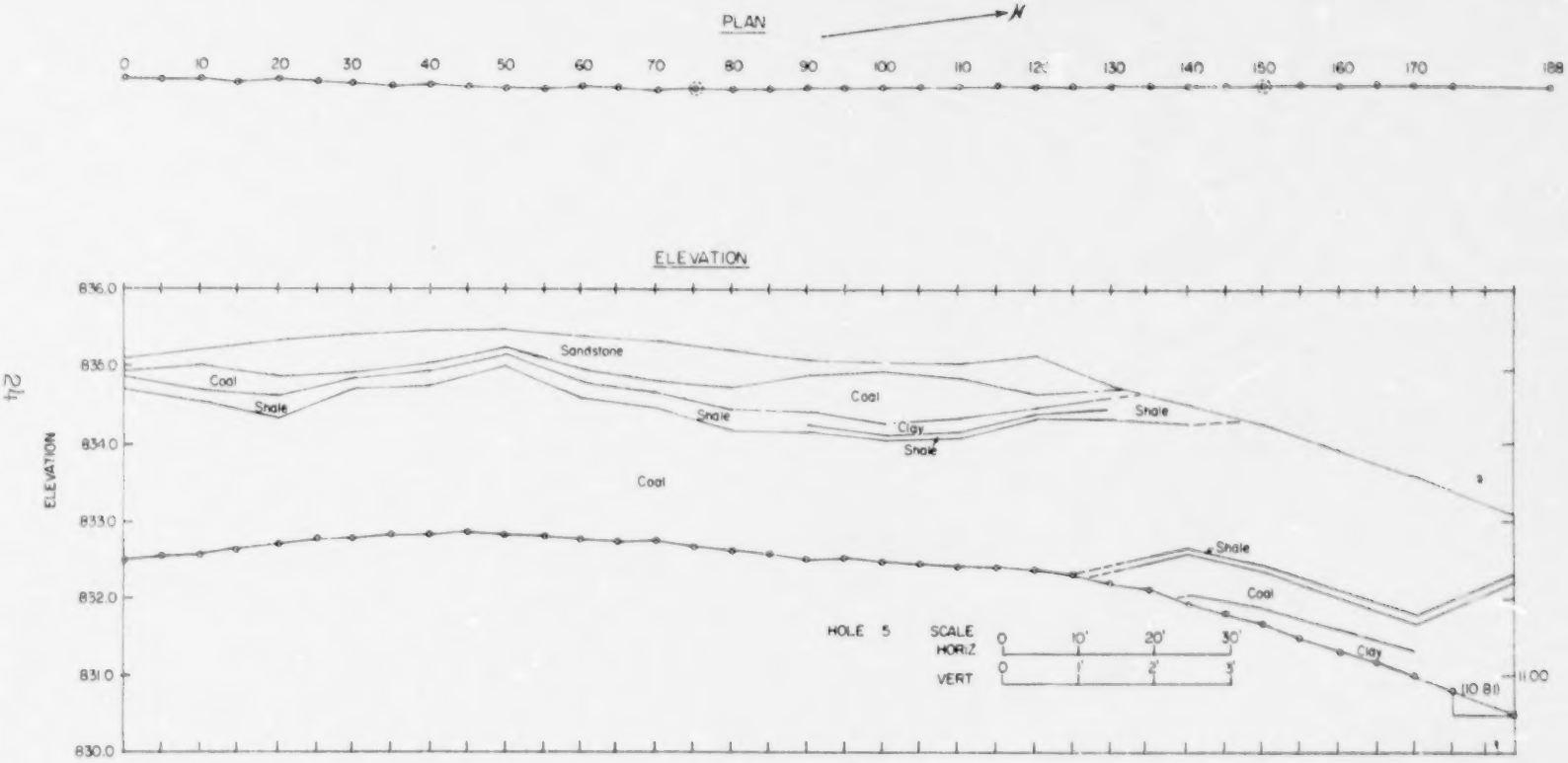


Fig. 11 - Plan and Elevation - Views of Hole No. 5

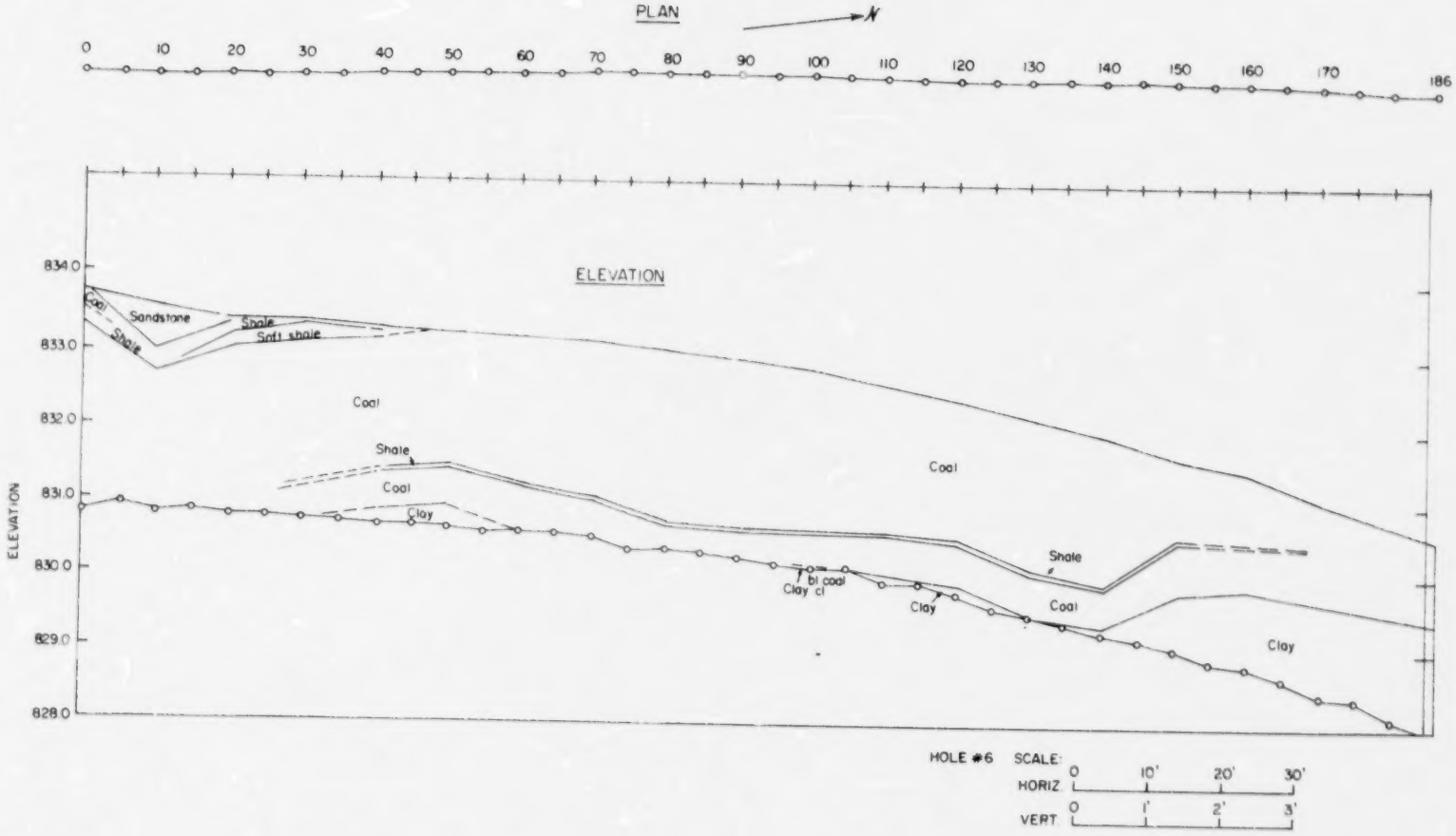


Fig. 12 - Plan and Elevation - Views of Hole No. 6

EXPERIMENTAL PROGRAM

For both the McDaniels drift mine and the auger holes, data were first collected to establish "base" flows and effluent quality. The "base" or reference condition for the McDaniels mine was the unsealed and continuously draining mine. Oxygen concentration in the mined-out volume was 21%, and the water ponded on the clay floor was estimated to be less than 300 gallons.

The original intent was to let all the auger holes drain continuously and monitor the discharges. However, the quantity of water ponded in the back of the holes--up to 3000 gallons in the case of Hole No. 6--meant that sudden changes in concentration of water flowing into the ponded water would be "swamped" by the ponded water, thereby further decreasing the response of the discharge to changes taking place within the mine.

The operating conditions finally selected for establishing "base" rates in auger holes 2A, 2B, 3, 4, 5, and 6 were the unsealed or open holes with 21% oxygen throughout, and the ponded water pumped on a weekly schedule. The flow rates reported for these holes were determined by measuring the volume of water pumped and dividing this volume by the time elapsed since the previous pumping. Hole No. 1 did not dip toward the back and had very little ponded water, so it was allowed to drain continuously for its "base" operating condition.

Variation in Oxygen Concentration

The atmosphere within McDaniels mine was controlled at different oxygen levels by: 1) the addition of pure oxygen; 2) constant air input; or 3) nitrogen purging. The time periods for these operational modes are given in Table II. Oxygen concentrations are plotted in Figure 13. An uncontrolled mode was also used in which the mine was closed as with a conventional "air seal" and the gas composition within the mine allowed to reach a steady-state value.

Table II. McDaniels Test Mine Operating Conditions

Time Period	Operational Mode	O_2 Conc.
Aug. 10, 1965 - Oct. 6, 1966	Base Conditions	21%
Oct. 6, 1966 - Aug. 1, 1967	Nitrogen Purge	1 to 2%
Aug. 1, 1967 - Nov. 18, 1967	Oxygen Addition	21 - 35%
Nov. 18, 1967 - Aug. 16, 1968	Air Purge	21%
Aug. 16, 1968 - Sept. 22, 1969	Air Seal	21 to 10%
Sept. 22, 1969 - Present	Nitrogen Purge	0.25 to 0.5%

Preceding page blank

Fig. 13 - Oxygen Concentration - McDaniels Mine

During nitrogen purge, a water manometer was installed with one leg open to the atmosphere and the other to the interior of the mine. A wire contact was set to operate a sensitive relay which controlled a magnetic valve on the nitrogen supply line. The wire contact maintained a slight positive pressure of approximately 0.5 mm H_2O in the mine.

The original manometric control used during the Oct. 6, 1966 to August 1, 1967, nitrogen purge was somewhat erratic since water vapor from the mine would sometimes condense in the tubing leading to the manometer or in the water of the manometer itself, thus changing the set point of the control. The redesigned manometer system had a slow nitrogen flow through the tubing connecting the mine to the manometer to prevent diffusion of water and subsequent condensation of water in the manometric system.

Test Holes

A number of small test holes were drilled around the periphery of the McDaniels mine to determine the environmental conditions at points well back of the worked face. These consisted of twelve vertical, one-inch diameter holes drilled through the overburden to the coal seam at varying distances up to 100 feet back of the mined volume. In only two cases was the section between sandstone and coal (the upper shale layer) tight enough to "hold" water used for drilling. Two holes were fitted with 1/4" aluminum pipe down to the coal and cemented in just above the shale overlying the coal. The pipe was capped in preparation for water and gas phase sampling.

Water was sampled by running sections of 3/16" brass tubing joined by leak-tight connectors, to the bottom of the holes. A serum cap was mounted on top of the string of tubing and water pulled into the tubing using a hypodermic syringe. Since the hole was over 30 feet deep in each case, water could not be drawn to the top, but the water contained in the tubing when withdrawn was adequate for analysis by atomic adsorption spectroscopy.

Gas samples were taken in the same manner, but due to the comparatively large gas volume of the tubing in relation to size of gas sample collected for gas chromatographic analysis, the values obtained for oxygen concentration are not believed to accurately represent conditions at the bottom of the hole. The procedure has been revised for future sampling.

Air "Permeability" Measurements

The McDaniels mine and auger holes were tested for air tightness or "permeability" by pressurizing the holes with air to 10 to 20 inches of water, then observing the rate of pressure decline. A cannister type vacuum sweeper was used as the air compressor. The seal on the McDaniels

mine was used without alterations except to plug the water trap during pressurization. The auger holes were tested with a packer-type seal. A truck tire inner tube was contained between two plywood disks of slightly smaller diameter than the auger holes. The circumference of the hole at the depth the seal was to be made was coated with patching plaster, the seal positioned and the inner tube pumped to 10-15 psi before the plaster hardened.

When testing auger holes 2A and 2B, two seals were required. Because the thin section between the two holes was highly permeable, seals were set in both holes at the same depth, and the pair was pressurized by adding air to either 2A or 2B. Pressure decline curves were obtained on both holes.

Derivation of the "permeability" value (K/V) from pressure decline data plotted as log ΔP vs. time is given below.

Change in moles of gas, dn, in constant volume, V, with change in pressure, dp, using the perfect gas law ($pV = nRT$):

$$Vdp = RTdn$$

From mass transfer equation:

$$dn = kA(P_o - P)dt$$

$$= K(\Delta P)dt$$

Substituting for dn and separating variables:

$$\frac{dp}{\Delta p} = \frac{KRT}{V}\,dt$$

Integrating:

$$\ln \frac{(\Delta P_2)}{(\Delta P_1)} = \frac{K}{V} RT(t_2 - t_1) = 2.3\ (\log \Delta P_2 - \log \Delta P_1)$$

but:

$$\frac{\log(\Delta P)_2 - \log(\Delta P)_1}{t_2 - t_1} = \text{slope of line on log } \Delta P \text{ vs. time plot}$$

so:

$$\frac{K}{V} = \frac{2.3(\text{slope})}{RT} = 0.1325 \times \text{slope}$$

$$\text{Units of } \frac{K}{V} = \frac{\text{Cu. ft. of air}}{(\text{hr.})(\text{cm. } H_2O)(ft^3)}$$

where:

V = volume of mine in cubic feet
R = gas constant = 751$(ft^3)$$(cm.H_2O)$/lb-mole,°R
T = Temp.,°R
P = Pressure in cm. of H_2O
t = Time in minutes
K = kA = "permeability" constant
n = number of moles
A = Cross-sectional area for mass transfer

Note: plot of log ΔP vs. Time; ΔP in cm. of H_2O, t in minutes

Analytical Procedures

Acidity (Total Acidity): Hot titration to the phenolphthalein end point was the method used to determine acidity. Values are reported as ppm (or mg/ℓ) calcium carbonate equivalent.

Sulfate: Sulfate was determined by standard gravimetric procedures such as those presented by Scott (3).

Total Iron: If only total iron was to be determined, the concentration was found using an Atomic Adsorption Spectrometer. If ferric and ferrous ions were to be determined, the total was taken as the sum of ferric and ferrous ions.

Ferrous Iron: The Zimmerman-Reinhardt method as described by Hillebrand (1), p. 396, using diphenylamine indicator, was applied to the sample as received.

Ferric Iron: The ferric ion was determined by reduction with titanous chloride using procedures described by Hillebrand (1) p. 398.

EXPERIMENTAL RESULTS

Discharges from the McDaniels mine and the auger holes are given as monthly averages of acid and sulfate discharge in Tables III and IV, and graphically in Figures 14 to 21.

Data collected on individual sampling dates are given in Tables VII through XIV in Appendix I.

The flow rates for the McDaniels mine from August, 1965, through December, 1967, were "corrected" using Figure 22. This was advisable since the drain from the air trap on McDaniels Mine was frequently plugged with "yellow boy" when the oxygen concentration within the mine was 10% or higher. The "corrected" flow was determined by noting the water level in Well No. 6, then using the flow rate corresponding to this level as given by Figure 22 as the "corrected" flow.

The air permeability of the auger holes was checked at various depths. As seen in Table V the difference in permeability with depth is usually less than the reproducibility of the permeability measurements. The values tabulated are the average of three or more measurements. For any one position, repeatability of pressure decline curves was good. However, use of patching plaster along the line of contact of the seal with the mine wall did not eliminate leakage behind the plaster through the more porous strata. This source of leakage was variable and unrelated to the depth of the seal.

Permeability measurements were made during the winter months when the overburden was relatively saturated (with water), thus the permeabilities are lower than if tested during the summer or early fall when the overburden is normally drier.

Preceding page blank

Table III. Average Monthly Acid and Sulfate Loads (lbs/day)

For McDaniels Mine

Month	Acid Load	Sulfate Load	Month	Acid Load	Sulfate Load
8/65	.1452		11/68	.1617	
9/65	.1767		12/68	.1806	.2865
10/65	.1968				
11/65	.2333		1/69	.2638	.3987
12/65	.2935		2/69	.4255	.6362
			3/69	.3254	.4892
1/66	.2839		4/69	.8457	1.1183
2/66	.4929		5/69	.6913	1.1437
3/66	.5032		6/69	.3402	.5726
4/66	.4567		7/69	.2245	.4193
5/66	.5710		8/69	.1342	.3605
6/66	.3022		9/69	.1077	.2420
7/66	.2994		10/69	.1150	.2222
8/66	.2222		11/69	.0925	.2118
9/66	.1520		12/69	.0820	.2035
10/66	.1328				
11/66	.1402		1/70	.1052	.2235
12/66	.1273		2/70	.1725	.3063
			3/70	.2823	.4658
1/67	.1256		4/70	.4167	.6123
2/67	.2679		5/70	.4955	.7010
3/67	.4935		6/70	.2582	.4978
4/67	.4200		7/70	.1710	.3306
5/67	.3677		8/70	1668	.3212
6/67	.2106				
7/67	.1183				
8/67	.0643				
9/67	.0760				
10/67	.1110				
11/67	.1478				
12/67	.1387				
1/68	.1910				
2/68	.3160				
3/68	.4204				
4/68	.7660				
5/68	1.3168				
6/68	.5596				
7/68	.4153				
8/68	.3797				
9/68	.2428				
10/68	.1856	.2970			

Table IV. Average Monthly Acid and Sulfate Loads (lbs/day)

For Auger Holes

	1		2A		2B		3	
Month	Acid Load	Sulfate Load	Acid Load	Sulfate Load	Acid Load	Sulfate Load	Acid Load	Sulfate Load
3/69	(Alk)	.3537	.0979	.1709	.0090	.0781		
4/69	.178	.7687	.2882	.4855	.0690	.2709	.3888	.6133
5/69	.1704	.6609	.3238	.4350	.0480	.2067	.3423	.4971
6/69	.1427	.4185	.1718	.2460	.0088	.0385		
7/69	.2619	.5564						
8/69	.1500	.4140	.0352	.0705	.0240	.0792	.0018	.1368
9/69	.0852	.2190	.0255	.0360	.0048	.0310		.0698
10/69	.0780	.2550	.0080	.0197	.0028	.0277	.0115	.0665
11/69	.0570	.2790	.0040	.0120	.0175	.0630	.0048	.0668
12/69	.0820	.4450	.0150	.0200	.0470	.1200	.0065	.0845
1/70	.2096	.6943	.1475	.2162	.0828	.1893	.2083	.5883
2/70	.1680	.5895	.3145	.3885	.0478	.1800	.8820	1.3490
3/70	.4413	1.0660	.4770	.5740	.0660	.2925	.6930	1.1115
4/70	.3843	.9310	.4170	.4825	.1250	.2758	.5863	.9607
5/70	.4820	.9527	.5500	.6900	.1300	.4050	.8700	1.5067
6/70	.2580	.5250	.1050	.1300	.0520	.1150	.1400	.3280
7/70	.2340	.4550	.0820	.1180	.0420	.1020	.0410	.2090
8/70	.3030	.5900	.1320	.1700	.1990	.3290	.1940	.3850

	4		5		6	
Month	Acid Load	Sulfate Load	Acid Load	Sulfate Load	Acid Load	Sulfate Load
3/69					.2224	.9402
4/69	.1657	.3205			.8215	2.1385
5/69	.4383	.8647	.0378	.2334	.9976	2.5283
6/69			.0278	.1451	.5973	1.5580
7/69					.4490	1.1450
8/69	.0060	.1455	.0120	.0927	.0570	.5480
9/69	(Alk)	.0880	.0163	.0880	.0493	.3333
10/69	(Alk)	.0800	.0210	.0813	.0210	.2198
11/69	(Alk)	.0880	.0250	.0840	.0240	.2403
12/69	(Alk)	.0840	.0445	.1265	.0450	.3500
1/70	.1345	.4893	.0398	.1040	.1370	.5586
2/70	.4483	.9690	.0573	.1453	.8887	1.6960
3/70	.3637	.7740	.0833	.1986	1.4890	3.5387
4/70	.4907	1.0690	.1067	.2403	1.3600	2.8300
5/70	.9325	1.7200	.3390	.5430	2.1300	3.6933
6/70	.1090	.5760	.0790	.2090	.7230	1.8000
7/70	.0310	.1730	.0460	.1250	.4060	.9770
8/70	.1216	.3620	.0600	.1400	.7180	1.4290

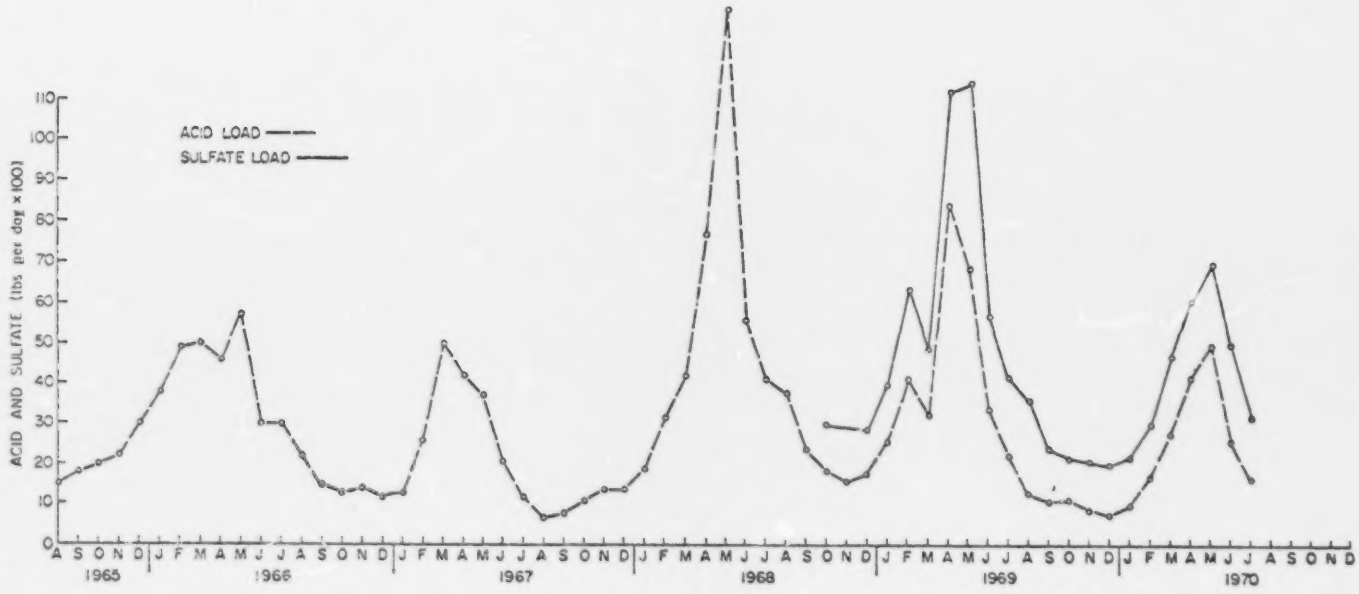


Fig. 14 - Monthly Average Acid and Sulfate Loads for McDaniels Mine

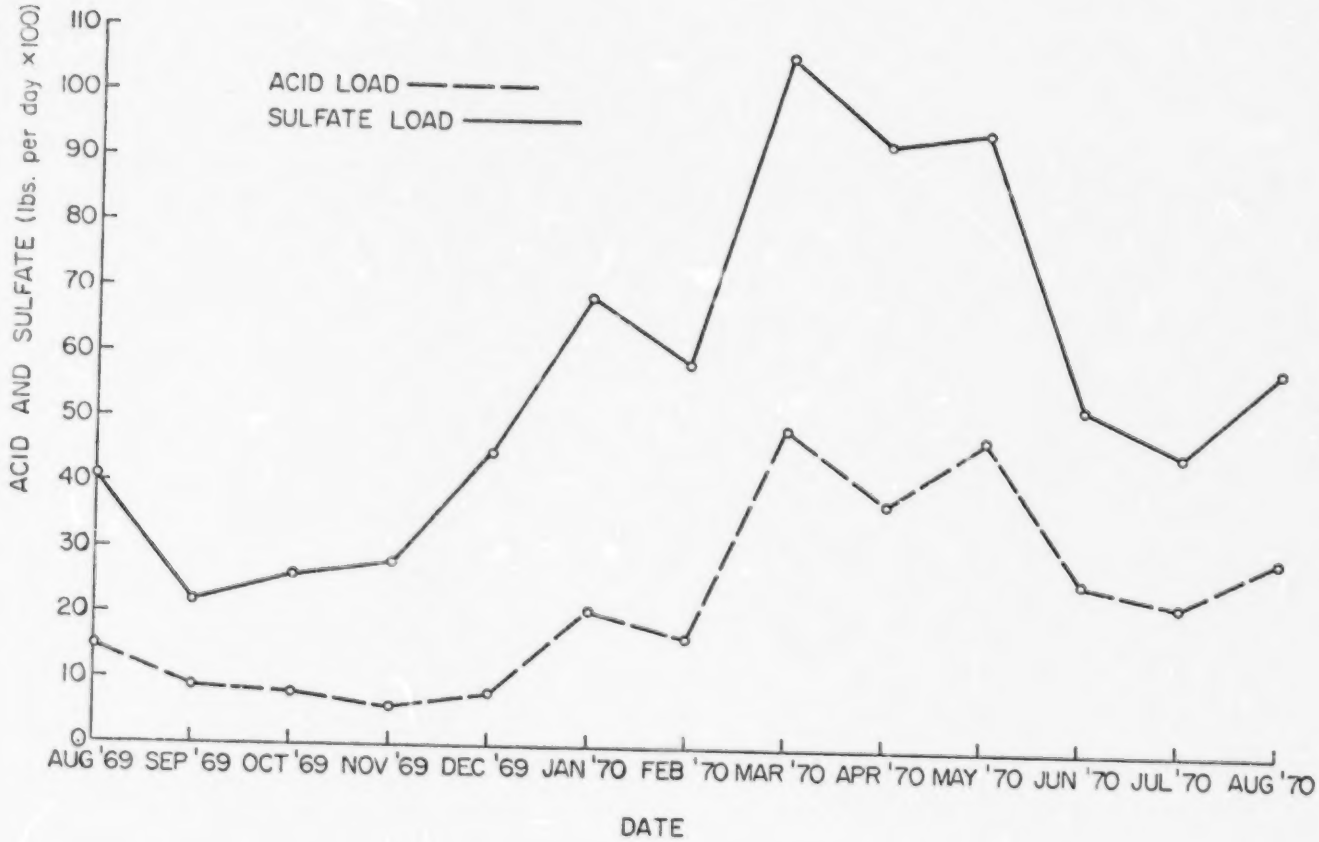


Fig. 15 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 1

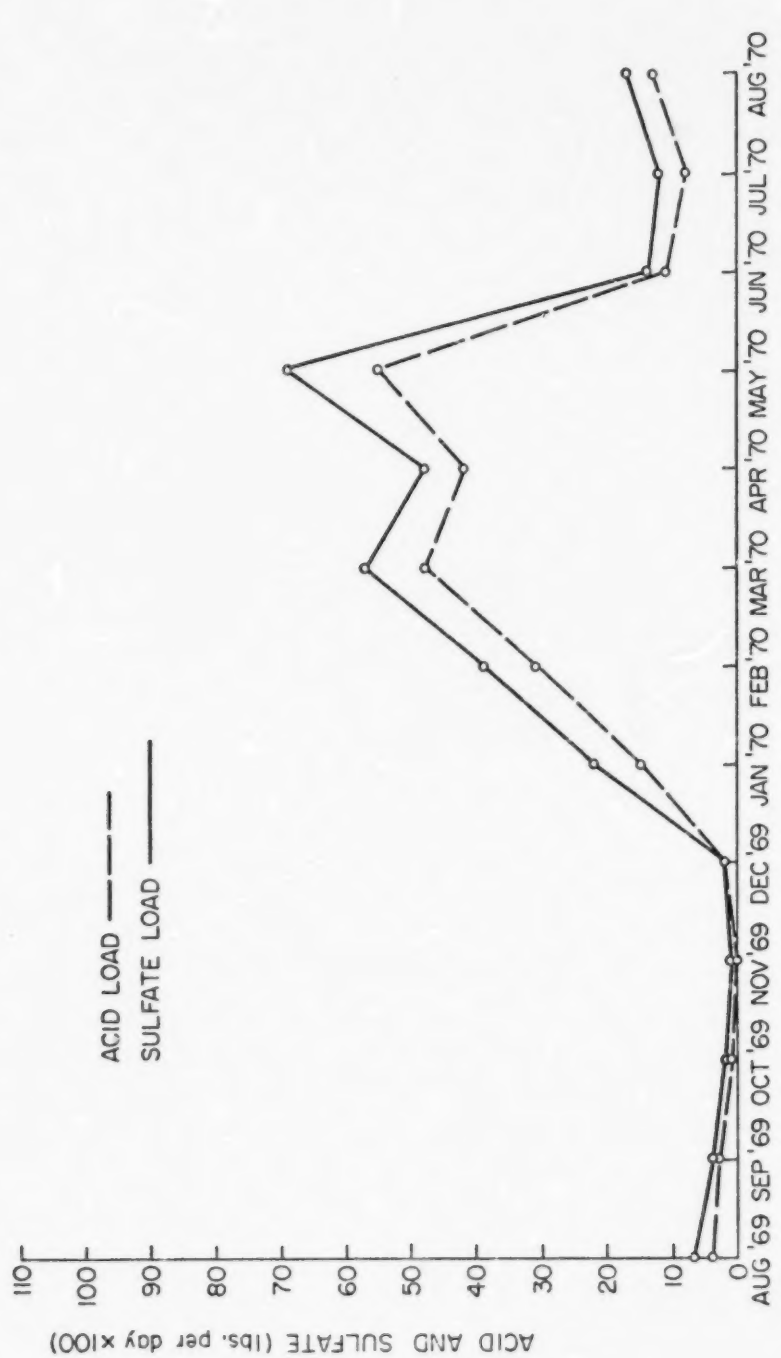


Fig. 16 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 2A

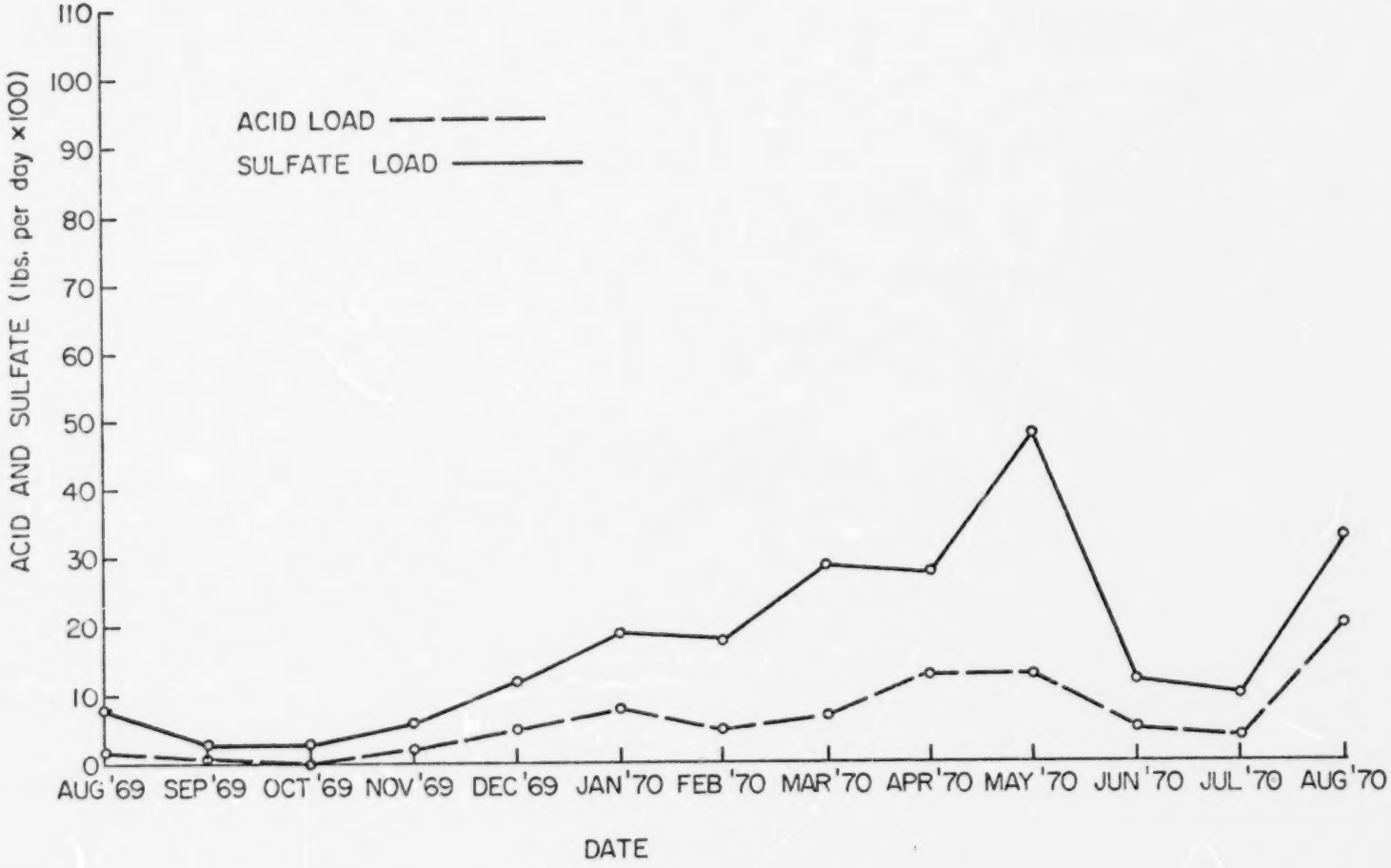


Fig. 17 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 2B

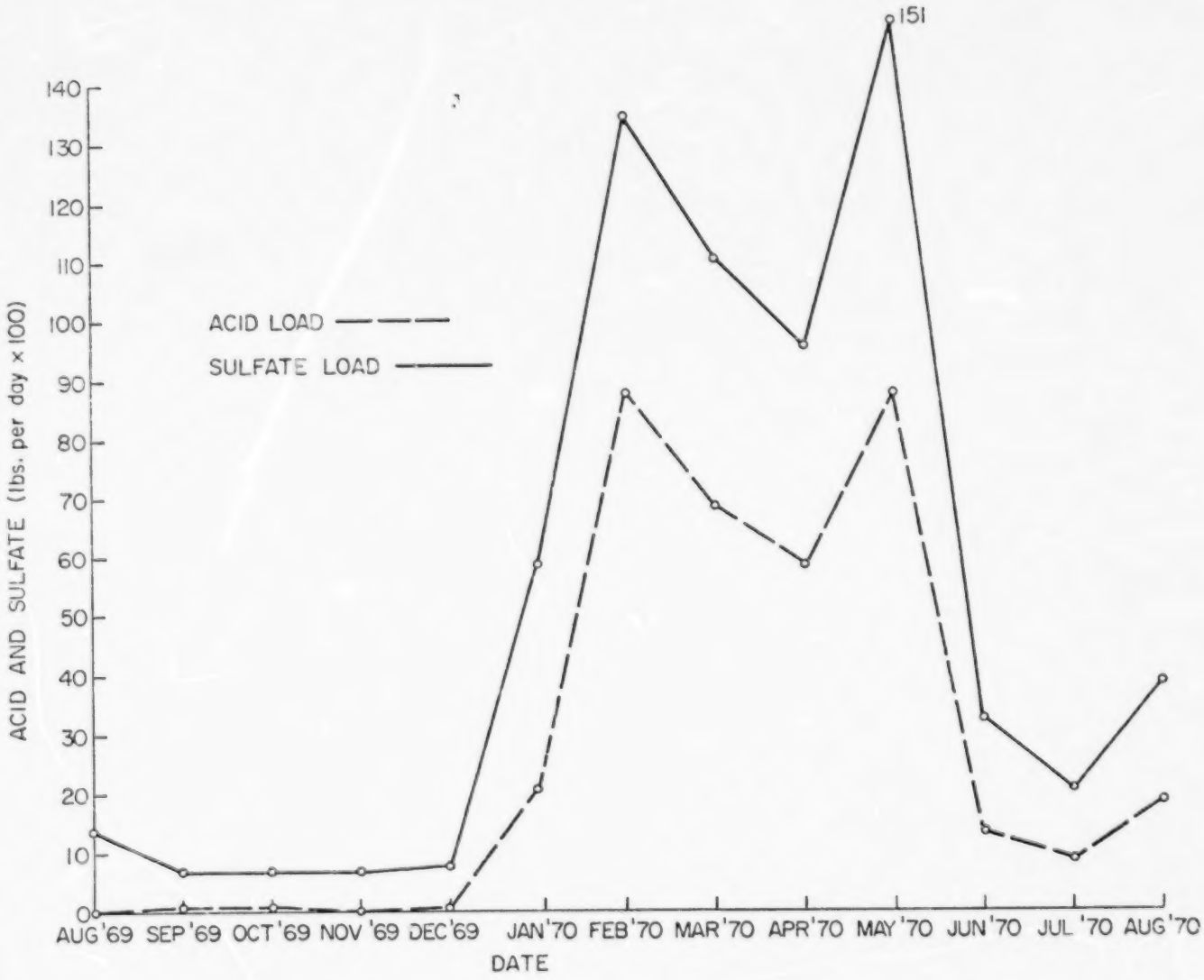


Fig. 18 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 3

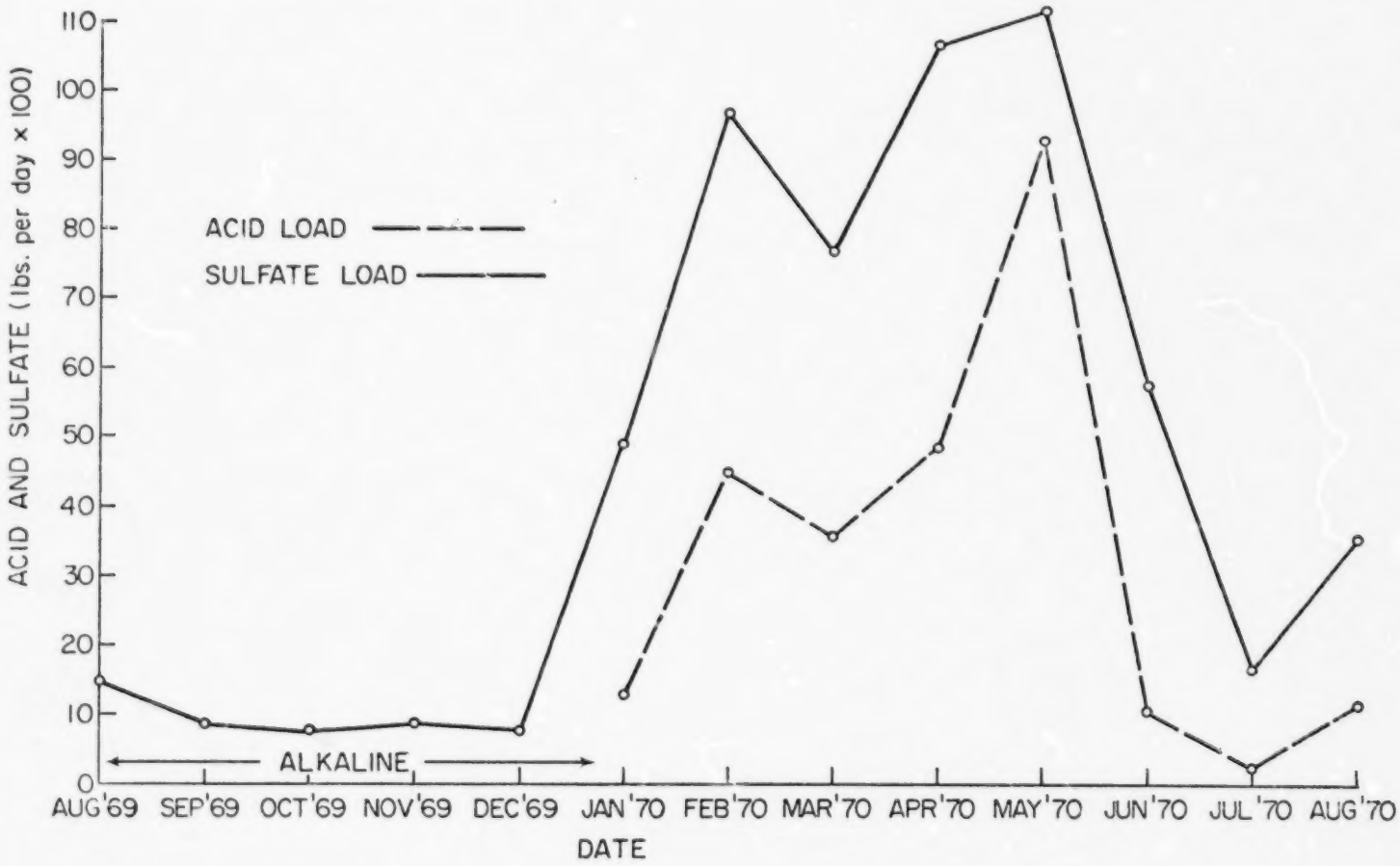


Fig. 19 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 4

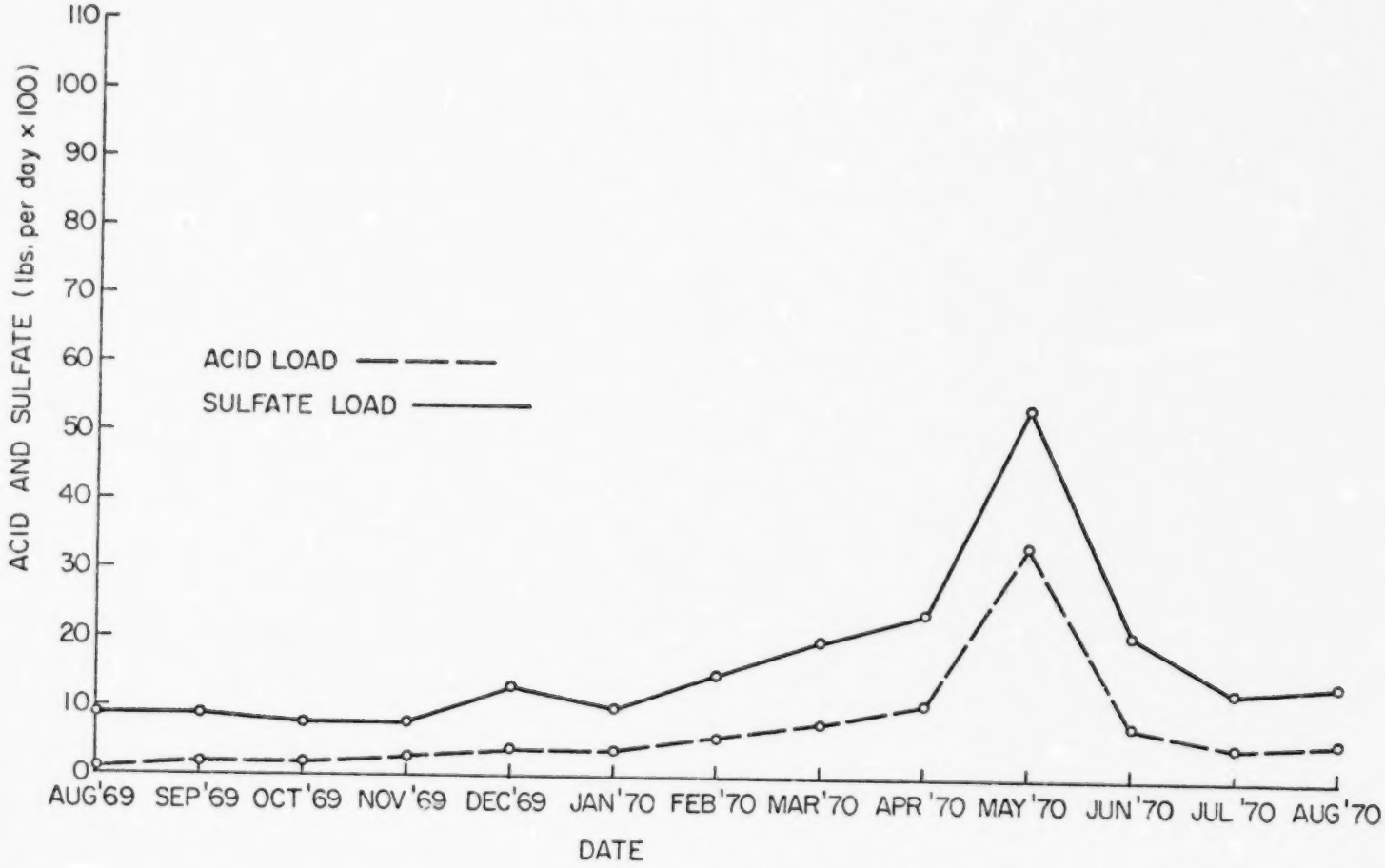


Fig. 20 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 5

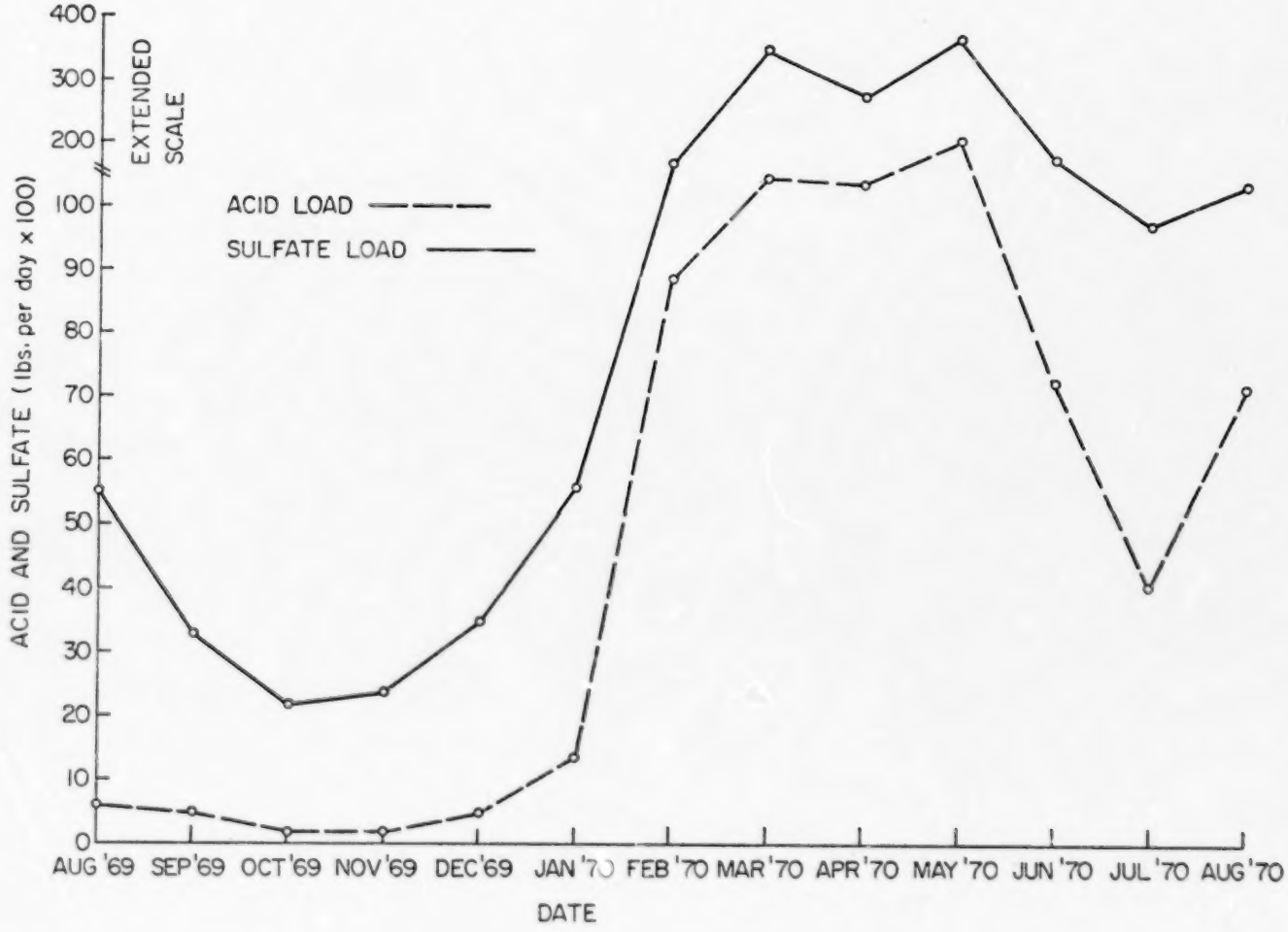


Fig. 21 - Monthly Average Acid and Sulfate Loads for Auger Hole No. 6

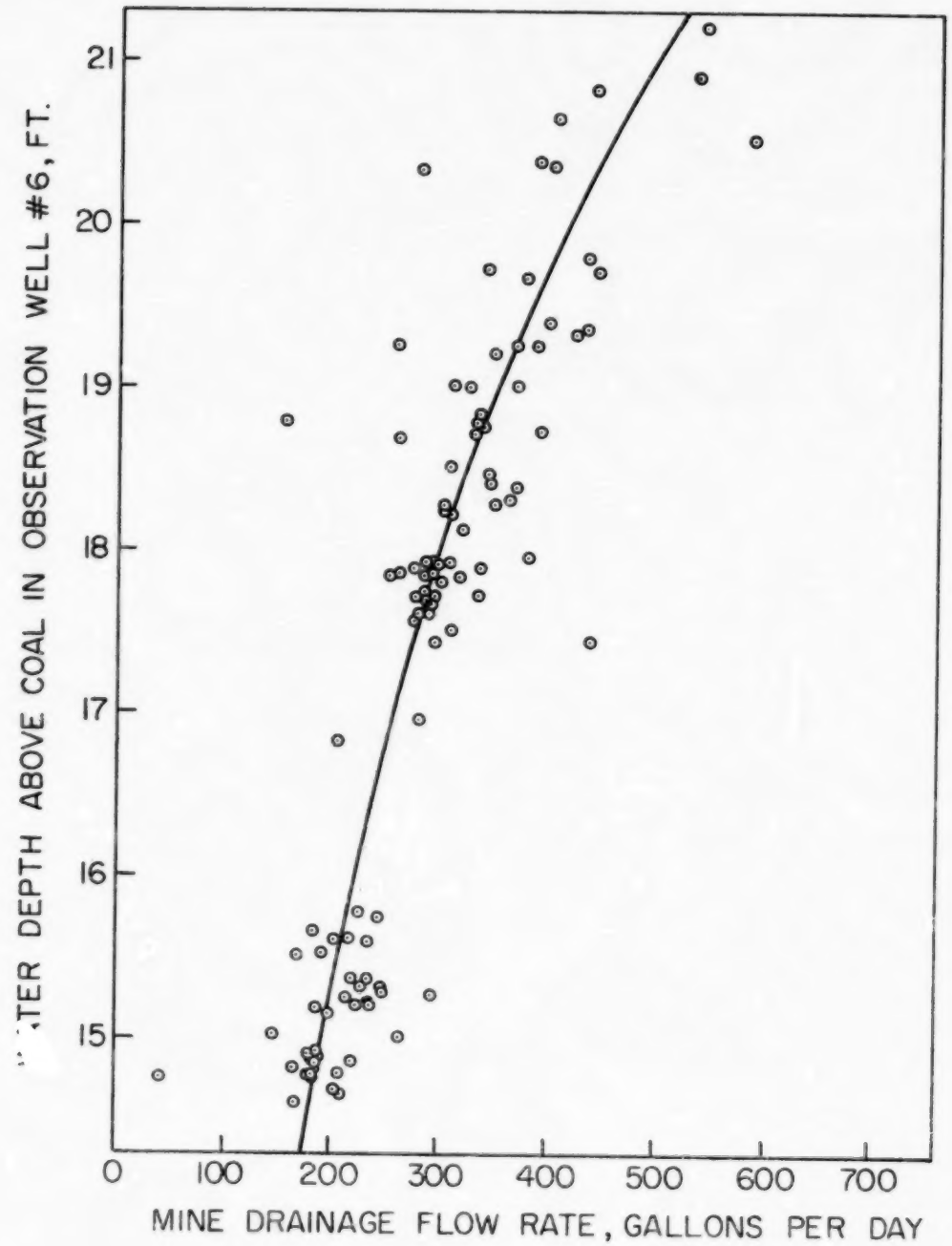


Fig. 22 - Depth of Water in Well No. 6 vs. Mine Drainage Flow Rate

Table V. Air "Permeability" Measurements

Hole No.	Depth of Seal (ft)	Slope of Plot (cm H_2O/min)	"Permeability" (K/V x 10^2)
1	85	0.12	1.6
1	27	0.19	2.5
1	87	0.095	1.3
2A	41	0.76	10.1
2B	4	0.43	5.7
3	13	0.69	9.1
3	30	0.73	9.7
4	22	2.3	30.5
4	43	0.48	6.4
5	7	0.93	12.3
5	41	0.24	3.2
6	30	0.30	4.0
6	57	0.32	4.2
McDaniels	-	0.068	0.90

DISCUSSION OF RESULTS

General

A few general comments should be made concerning effluent data from McDaniels mine and the auger holes. For the purpose of this project, we are interested in monitoring that value which will give the best measure of the quantity of pyrite oxidized. According to the stoichiometry usually quoted for the oxidation of pyrite, either sulfate or total acidity might be used to measure products of oxidation. Practically, the non-titratable calcium and magnesium should be included in the equivalent acidity to arrive at the stoichiometric quantity of total acid.

For older, stabilized pyritic systems such as the McDaniels mine, either total acidity or sulfate content of effluent waters appears to be a reliable indication of pyrite oxidation products contained in the effluent water. For the newly drilled auger holes, total acidity alone is not adequate. Calcite inclusions, together with the "buffering" or ion-exchange capacity of freshly exposed clay, "neutralize" the acidity produced, resulting in "alkaline" discharges with high sulfate contents. A more reliable estimate of pyrite oxidation is given by the sulfate analysis although there is, no doubt, some sulfate produced in the breakdown of clay minerals by acid waters. Sulfate is also lost in the precipitate found on the floor and in flow channels of the mine. These precipitates contain iron hydroxy-sulfates of variable compositions.

The above discussion implies that the initial acidity data from the auger holes are not a reliable indication of pyrite oxidation products in the effluent. Later data show a more consistant relation between total acidity and sulfate content.

To assist in understanding the interpretation of data and discussion of results given in this section, a conceptual model of an underground pyritic system is described in the following paragraphs. This model was developed from basic reaction kinetic studies described by Smith and Shumate(6) together with observations made in conjunction with the project discussed herein. At this point the model is presented without experimental justification. The interpretation of data leading to the formulation of the conceptual model and experimental evidence proving its validity are given in the following sections.

Conceptual Model of Underground (Drift) Mines

"Acid" production rate or "acid" load from an underground mine is determined from flow rate and acid (or sulfate) concentration of the mine's discharge. The observed rate of production is the result of two independent processes: 1) rate of acid formation (or rate of pyrite oxidation)

Preceding page blank

and 2) transport of oxidation products to the discnarge waters.

Pyrite Oxidation

The pyrite oxidation reaction will be examined first. There are two factors which may determine oxidation rate, depending on which is controlling: 1) the chemical reaction and/or 2) rate of transport of reactant (oxygen) to the reaction site. Before this concept can be explained, the "reaction site" must be defined. Basically it is an exposed pyrite surface together with the gas, liquid, and solid interfaces at this surface. Its characteristics are described by the interfacial area per unit volume of pyritic material and the conditions at this surface, i.e. oxygen concentration, ferric/ferrous ratio (as determined by number and activity of bacteria), temperature, etc. In other words, the reaction site consists of those factors described by Smith & Shumate (6) which determine the rate of pyrite oxidation.

Oxidation rate is either (approximately) first order (i.e. varies directly with oxygen concentration), or it is zero order down to 2 or 3 percent oxygen, depending on whether the oxidation is predominately chemical (first order) or biological (zero order). Below 2 percent oxygen, the rate is first order in respect to oxygen in both biological and chemical systems. Regardless of the nature of the reaction, a finite concentration of oxygen must be present at the pyrite surface before the pyrite surface can be termed a "reaction site".

Assuming the mined-out volume of a mine has an oxygen concentration of 21 percent, reaction sites will be exposed to oxygen concentrations varying from 21 percent at the working face to 0 percent back into the coal strata. The oxygen concentration gradient in a particular stratum will depend on the void volume (porosity), the exposed surface area of pyrite per unit volume of the stratum, and the order of the chemical reaction. The calculation of the oxygen concentration gradient is simply a problem of diffusion plus chemical reaction for which quantitative mathematical solutions are available.

Note that "reaction sites" extend as far into the strata as oxygen diffuses. The greater the void volume, or porosity, of a pyrite-containing stratum, the greater the rate of oxygen diffusion because of the larger cross-sectional area available for diffusion. At the same time, more pyrite surfaces will be exposed in a porous material simply because of the greater total surface exposed to the vapor phase. Conversely, the tighter the formation, the lower the quantity of oxygen which will diffuse through it, and the less oxygen available for oxidation per unit volume of material.

Since oxygen diffusivity in water is 1×10^{-4} that in air, essentially all oxygen must be transported to the reaction site as a vapor. Diffusion through water is too slow, and the quantity of dissolved oxygen in water entering an underground mine is too small to produce a significant "acid"

load. The diffusion mechanism therefore helps define the location of reactive sites: they are exposed to vapor; they can not be submerged under more than a quarter inch of water, or more precisely, there can not be more than the equivalent of a quarter inch of stationary or laminar flowing water between the pyrite surface and the source of oxygen through which oxygen must move by molecular diffusion or diffusion of oxygen becomes rate-determining.

Another fact is brought out by the conceptual model that must be kept in mind when interpreting discharge data: the quality of effluent water is not directly related to the quality of water at reaction sites. That is, discharged water does not describe the aqueous environment at reaction sites in terms of concentration of oxygen, oxidation products, ferric/ferrous ratio, or other factors influencing the oxidation rate. The water in contact with most reaction sites has a high concentration of oxidation products, probably at or near saturation. The discharge water is a mixture of these waters from reaction sites and the ground water entering through major flow channels. The ground water usually contacts few if any reaction sites.

Removal of Oxidation Products

The rate which pyrite oxidation products enter the effluent stream is determined by three basic mechanisms:

1. Flushing by a rising water table.

2. Percolation by water flowing down through open channels or fractures during or after periods of heavy precipitation.

3. Diffusion or "weeping" of saturated solutions of reaction products caused by water condensing on reaction sites due to the lowered vapor pressure of the highly concentrated solutions at these locations.

The particular removal mechanism (or mechanisms) involved at a specific reaction site will depend on its location in respect to the water table and/or flow channels through which water percolates. If a reaction site is isolated from these sources of direct removal, oxidation products will build-up until the degree of saturation at the site and surrounding area is high enough that the rate of transport to points of direct removal by percolation or flushing is equal to the oxidation rate. The build-up of oxidation products has no effect on the oxidation rate (6).

Obviously the instantaneous rate of oxidation product removal is independent of the rate at which the oxidation products are formed. At steady state conditions the long term rates are equal; that is, over a three or four year period, the total amount of oxidation products removed will be equal to the total amount of oxidation product formed, but the daily or weekly acid loads as measured from the discharge cannot be related to the rate of pyrite oxidation.

All three of the above removal mechanisms have been observed either in the laboratory or in the mines. The flushing and percolation mechanisms are self-evident. The diffusion, or "weeping" process is too slow to be observed directly. To determine its effectiveness as a transport mechanism the "weeping" rate was measured in the laboratory by supporting a (roughly) 120 cc. cube of coal several inches above a layer of distilled water in a vented flask. After allowing several months for the system to reach steady-state, the water was analyzed for acid and sulfate content and the experiment resumed. Several months later the water was again analyzed yielding the results given in Table VI.

Table VI. Experimental "Weeping" Rate

Component	Rate of Transport (mg/day)	Rate of Transport (μg-mole/day)	Equivalent* Oxygen (μg-mole/day)
Acidity	5.5	55	96
Sulfate	4.2	43	74

*Oxygen required to produce the acidity (or sulfate) by oxidation of pyrite

A large Warburg-type apparatus was used to determine oxygen up-take rate for the same sample. The rate of oxygen consumption was 80 ± 20 μg-mole/day, the same, within experimental error, as the Equivalent Oxygen shown in Table VI. These data show that at steady state, the diffusion or "weeping" mechanism will transport reaction products from reaction sites at the same rate they are formed. Of course, the time to reach steady state depends on the distance and diffusion path between the reaction site and the receiving water.

Physical Model

Keeping in mind the concepts discussed above, a physical model of a drift mine such as the McDaniels Mine or the auger holes can be described. Referring to Figure 23, the oxygen concentration gradient (and therefore relative oxidation rates), and removal rates can be qualitatively evaluated in relation to boundaries fixed by the working face of the mine, the extent of oxygen diffusion, and the water table.

To illustrate the situation which exists in each more or less homogeneous geologic stratum let us examine the shale parting which occurs between the sandstone overburden and coal measures.

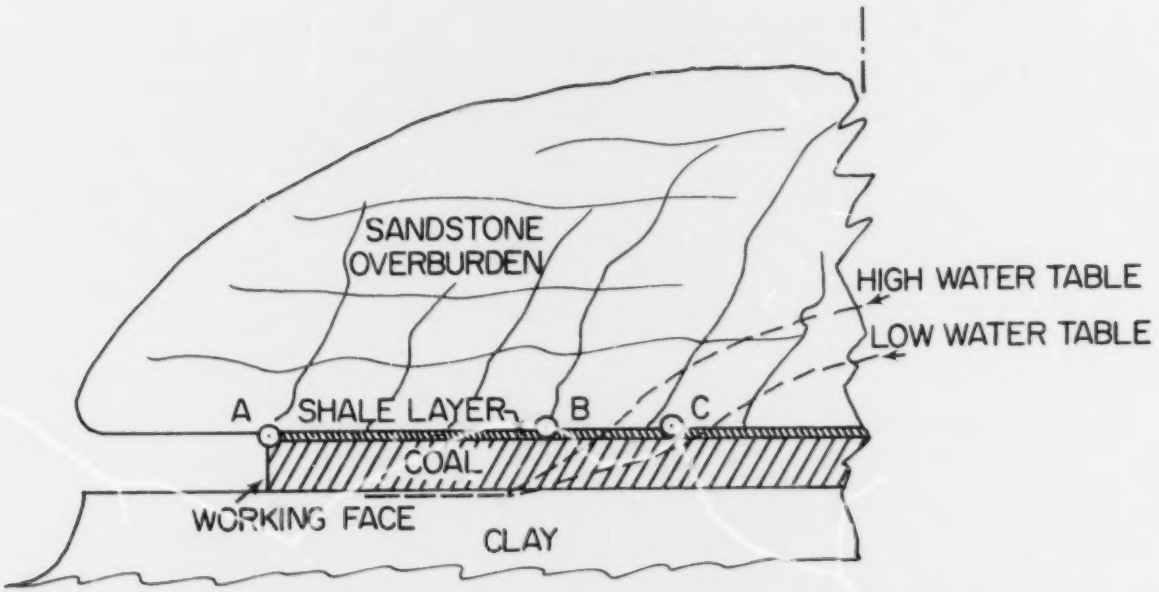


Fig. 23 - Model of Underground Pyritic System

At reaction site "A", oxygen concentration is essentially the same as in the mine, but as we move back into the shale parting toward "B", diffusion of oxygen cannot keep up with the consumption of oxygen by the oxidation reactions, so that the concentration of oxygen decreases. Note that reaction sites "A" and "B" are exposed to a vapor phase*; that is, there is a continuous vapor path to the source of oxygen and the reaction site itself is exposed to vapor. Oxygen can, therefore, be transported to these reaction sites through the vapor phase.

Point "C" on the other side of the high water table, is under water of essentially zero dissolved oxygen during the high water period. Under these conditions no oxidation occurs and point "C" is not a reaction site. During the low water period, if oxygen diffusion is sufficient to supply oxygen to point "C", oxidation will occur at this point.

Removal of oxidation products from each of these reaction sites is by different mechanisms. "A" is not near any water source that provides direct removal. The slow diffusion of saturated solutions from "A" by

*The so-called "vapor phase" oxidation does not imply the absence of liquid water which, according to Smith and Shumate (6) must be present before oxidation can proceed. At the near 100 percent relative humidity which exists in an underground mine, the pores and capillaries of the pyritic material are full of a saturated aqueous phase.

the "weeping" mechanism eventually carries the products of oxidation to the effluent stream. Point "B" is on the extension of a fracture in the sandstone overburden which is a water flow channel during periods of heavy precipitation. Oxidation products are periodically washed from "B" and carried by the percolation mechanism to the effluent water.

Point "C" is flushed of its oxidation products as the water table rises and falls during the hydrological year. Oxidation products do not build up to the extent reached at Point "A" which is never subjected to direct removal by water, but do reach a higher concentration than Point B which is washed by percolation at more frequent intervals.

Reaction site "B" as defined in this discussion is a very unique point. Most reaction sites would not be on a flow channel, but some distance away--varying from a fraction of an inch to several feet--from direct contact by flowing water. In other words, the overall removal rate of oxidation products from most sites is a combination of mechanisms: diffusion and percolation, plus flushing if affected by rise and fall of the water table.

The data collected from the auger holes and McDaniels mine will be discussed within the framework of this brief, qualitative description of kinetic factors which affect acid discharge.

Auger Holes

The outstanding feature of the discharge data from the seven auger holes is their individuality. Although one might expect Holes 1, 2A, and 2B to be different, Holes 3, 4, 5, and 6 are about as physically identical as one can reasonably expect. However, large differences in flow rates and acid concentration were observed. Acid and sulfate loads were not as different as flow rates or concentrations taken individually, but here also the differences were greater than anticipated.

The most unique auger hole is No. 5. Flows (see Table XIII) are much lower than Holes 4 and 6 which are located on either side of No. 5. The probable explanation is that Hole 5 stays in the coal or, in other words, above the clay for almost all of its length, contrary to holes 4 and 6. The reason this influences discharge rates is explained below.

Observations made in mines and auger holes in the Middle Kittanning (No. 6) coal, as well as reports of miners who have worked the area, indicate that the major water flow into the mines is through partings between the coal and clay bottom. It may be seen from Figs. 10, 11, and 12 that only the last 50 feet of Hole 5 intercepts this water flow between the coal and clay, while in Holes 4 and 6, over 120 feet are in the clay. Also the coal seam is more highly fractured near the front of the auger holes, so that the water flow from the sandstone overburden through the coal to the coal-clay parting would be greater near the entrance, where Holes 4 and 6 are in the clay and Hole 5 is entirely in the coal.

The only obvious relationship among the holes is the relative seasonal change in flows, concentration, and acid loads (see Figs. 15-21). While absolute values differ greatly, the shapes of the curves, or relative acid loads, are similar.

Effect of Asymmetry

With the general slope or dip of strata which exists in this area as evidenced in Figures 6 through 12, there will be some degree of nonuniformity or nonsymmetry in drainage areas covered by the auger holes.

For example, all other factors being equal, Hole 4 will drain more area on the up-dip side of the hole than on the down-dip side. The degree of drainage asymmetry will depend on the level of the water table between the holes as well as the entry point of water into the holes. If highly asymmetrical, the drainage into (for example) Hole 4 could originate from pyritic material oxidized by oxygen entering from Hole 3. Since lateral diffusion of oxygen or other gaseous components would be symmetrical about the center-line of the auger hole it enters, and drainage is not symmetrical, the effect of a change in gas phase composition imposed in one auger hole may influence the discharge of the hole on the down-dip side. Although we do not believe the drainage asymmetry is great enough to produce a significant distortion in acid or sulfate loads in two adjoining holes, this possibility will be checked when the holes are sealed by adding a gaseous tracer such as helium or ethylene oxide to Hole 4 and determining the relative amount dissolved in the discharges from Hole 3, 4, and 5-6 (see below). If the quantity discharged from 3 and 5-6 are the same, there is no effect of asymmetry on drainage. If there were none of the tracer in Hole 3 and as much in 5-6 as in Hole 4, this would indicate all drainage down-dip of Hole 4 goes to 5-6.

Another way of estimating the relative drainage area serviced by each hole is in terms of acid or sulfate load (as lbs/day) from each hole. The penetration of oxygen into the different pyrite-bearing strata will be symmetrical about the center line of the hole, the depth of penetration depending on the oxidation rate, oxygen diffusivity, and porosity of the strata. Oxygen penetration and therefore pyrite oxidation will be shown (see Section 7D) to extend at least 15 to 25 feet into the hill. The extent of oxygen penetration may be termed the hole's "reactive volume". This "reactive volume" should be proportional to the hole depth since oxygen diffusion rate is essentially uniform in a specific stratum throughout the test site. If drainage were also uniform, the acid load from the holes would be proportional to depth of the hole since the same drainage area would produce the same acid load in the discharge.

Sulfate loads are approximately proportional to depth for Holes 1, 2A, 2B, 3 and 4, indicating reasonably uniform drainage. However, when Holes 5 and 6, which have the same depth, are compared, the sulfate load from Hole 6 is from five to ten times greater than Hole 5.

If Holes 5 and 6 are considered as a unit, that is if the sulfate load from Hole 5 plus Hole 6 is compared to that from the other holes, the combined sulfate load is approximately that which would be expected for a 200 ft. plus 200 ft. = 400 ft. hole. The fact that Hole 5 does not enter the clay until the last 50 feet, and therefore does not intercept the major water flow path as explained above, probably accounts for the difference in drainage area serviced by Hole 5 and Hole 6.

Based on these observations, it is possible to use the holes as sets as originally intended; i.e. as comparable experimental units. Set A would be Holes 1 and 2A-2B and Set B Holes 3, 4 and 5-6. One hole from each set could be used as a reference hole and the others used for different experiments.

Steady-State Conditions

Data from the auger holes show that they have not yet reached steady-state conditions. Acid loads for corresponding periods of the hydrologic year are increasing drastically (see Table IV). Considering the response time observed in the McDaniels mine (see Section 7D) steady state is not to be expected for several years. In the case of the auger holes, build-up of oxidation products in areas not subject to periodic flushing has not reached the point where the removal mechanisms have attained a yearly rate equivalent to that of formation. Until the removal per year is equal to the yearly formation, annual acid and sulfate loads will increase.

It would be ideal to collect base rate data for several years until steady state conditions are reached. However, valuable time would be lost. Therefore we recommend that three of the five units available be used as "reference" mines, rather than only one, as originally proposed. By this means it will be possible to correct for the changes in relative acid loads which will occur. With the non-uniform drainage patterns observed, relative acid loads will change during the approach to steady state since areas of higher oxygen concentration will reach steady-state concentrations of oxygen products more rapidly than remote areas. Therefore the holes servicing the high oxygen areas will not only reach steady-state sooner, but their relative sulfate loads, compared to that of the slower holes, will change with time. Thus the concept of comparable experimental units is not valid unless this change in relative sulfate loads is determined by using two and preferably three holes as reference mines. While this procedure may not provide quantitative answers to change in relative loads, it will at least provide an indication of the error introduced by assuming a constant ratio of sulfate or acid loads.

McDaniels Mine

Discharge data from McDaniels mine show a surprisingly slow "time response" to imposed changes in atmosphere within the mine. When the plan to maintain a continuous positive pressure of nitrogen was first conceived, we

expected that results due to the change in oxygen concentration would reach steady state values in a few months. Data collected to date indicate this time period will be several years. For example, the McDaniels mine has been maintained at less than 1 percent oxygen since September, 1969--one year, at the time of this writing. Acid loads have decreased to 60 or 70 percent of the values observed during corresponding flow periods of the previous year. This is approximately one-half the decrease to be expected when steady-state is reached. Maintaining less than 1 percent oxygen concentration in the vapor phase should cause the acidity of the discharge to drop to a relatively constant value under 25 ppm. Referring to Table III, this would correspond to an average acid load varying from 0.10 lb/day for the high flows in May, to 0.04 lb/day for the low flows in late Fall. The figure of 25 ppm acid is based on 2 to 3 ppm dissolved oxygen in ground water entering the pyritic material around the mine, plus oxidation due to the (less than) 1 percent oxygen in the mine.

The mine and its "reactive volume" may be considered a storage area for pyrite oxidation products. If all oxygen to the mine could be eliminated so that no further oxidation would occur, the removal of stored products may be approximated by the familiar "exponential decay" curve. Assuming that 40 percent of the remaining products are removed per year as indicated by the past year's data, four and one-half years would be required to remove 90 percent of the oxidation products present at the time oxygen was eliminated from the mine.

Referring to the conceptual model described in Section 7B, the time response data confirm that the majority of reaction sites are not on or near water flow channels feeding the effluent stream, but are instead some distance away from flowing water. If the reaction sites were located where direct removal of oxidation products occurs, time response would be measured in weeks rather than years. These data also confirm the "vapor phase" oxidation concept; that is, the reaction sites are exposed to a vapor, rather than a continuous liquid, phase. Since one-quarter inch of water offers the same resistance to molecular diffusion as one mile of air, mass transport kinetics require a vapor phase transport path for oxygen. Oxygen transport rates in a submerged liquid environment are too low to account for the acid loads observed in McDaniels mine or the auger holes.

The concentration gradient of oxygen indicated by the model has also been observed both directly and indirectly. Air samples taken from drill holes 40 feet back of the coal face show a definite oxygen concentration, although the actual numerical values are not quantitatively reliable. Change in water quality with distance from the working face is also an indication of the oxygen concentration gradient. Water taken from Well No. 6 (see Fig. 1) 120 feet from the working face is essentially the same as ground water in the area; pH = 6.0, alkalinity = 10 ppm, sulfate = 55 ppm, while the water sampled from Well No. 2, 30 feet from the face, taken at the same time, had a pH = 5.8, acidity of 15 ppm, and sulfate of 125 ppm. These data demonstrate that pyrite is being oxidized

in remote areas, well removed from the working face of the mine, accessible only to oxygen transported through the vapor phase. The quantity of dissolved oxygen in ground water is too small to account for the amount of oxidation products found in the water from the wells or bore holes.

Principle Reaction Zone

The zone of greatest reactivity in the Middle Kittanning (No. 6) coal seam is the shale layer between the sandstone overburden and the coal. This strata contains 9 to 16 percent (as %S) pyritic sulfur. But more important, this shale layer has a high void volume, or porosity, as observed during drilling operations when drilling water was lost as soon as the shale layer was entered. With the high void volume, oxygen diffusion through this strata is high. The exposed surface of pyrite per unit volume of shale would also be high due to porosity and high pyrite content. In addition, the shale layer is the uppermost pyrite-containing strata so that more of it would be above the water table than any other pyritic strata.

Removal of Oxidation Products

The individual sample data (Appendix I) provide further information on the location of reaction sites and mechanism of product removal. Although not entirely consistent, the acid or sulfate load is generally more constant than either flow rate or concentration over a one or two week period. This is due to the essentially constant diffusion or "weeping" rate for transport of oxidation products to the effluent stream. Although the solutions transported by diffusion are saturated, they are diluted by water percolating through the flow channels which intercept the diffusion paths. This water is further diluted by water entering between the coal and the underlying clay to produce the final discharge. An increase in water flow into the mine, such as might occur after a day or two of light rain, will simply act to dilute the normal, steady flow of oxidation products and the acid load will stay nearly constant. However, if heavy or prolonged precipatation occurs so that secondary flow channels are used for percolation and the water table rises, then a greater portion of the reactive volume is subject to direct removal by flowing water, the diffusion paths from reaction sites are shortened and the acid loads will increase. This is the situation which exists in the Spring when acid loads reach their maximum values. As water flows recede, fewer flow channels are used, the water table drops, diffusion paths again lengthen, and acid loads reach their minimum values until a "steady-state" diffusion rate is again established. This accounts for the low acid loads in late Summer and early Fall seen in Figures 14 through 21.

Microbiological Effects

From the standpoint of biological catalysis, two important environmental conditions which exist at the reaction sites are;

a) relatively little water compared to surface area of pyrite exposed, i.e., low water-to-pyrite ratio, and

b) highly concentrated, high acid solutions in contact with pyrite.

Both of these conditions make it difficult to believe that microbial catalysis of pyrite oxidation can be a significant factor in the formation of acid mine drainage. As pointed out by Smith and Shumate (6), oxidation of pyrite may occur by two independent mechanisms: 1) Oxygenation, in which oxygen is directly adsorbed on a pyrite surface and becomes the immediate oxidizing agent (electron acceptor), and 2) ferric ion oxidation in which ferric ions produced in solution by aerobic microbial activity are adsorbed on the pyrite surface and become the immediate oxidizing agent. For the oxygenation reaction the major variable (for a given pyrite surface area), is the partial pressure of oxygen. At low pH's neither pH nor solution concentrations have a significant effect or oxygenation rate. For the ferric ion oxidation reaction, the rate of pyrite oxidation is determined by the ferric/ferrous ratio in solution as well as solution concentration and pH (see Ref. 6 for a more detailed discussion of the kinetics of this reaction).

Lau, et al.(2) have shown experimentally that both low water-to-pyrite ratios and a high concentration of acid and salts in solution reduce the number and activity of bacteria to the point that the ferric ion oxidation of pyrite is insignificant compared to oxygenation. Both of these conditions pertain to reaction sites in underground mines where, as shown above, vapor phase oxidation must be involved.

At first glance, it would appear that the importance of microbial oxidation could be quickly and positively identified by simply analyzing the solution at the reaction site, i.e.,the water in contact with the pyrite surface. However, such an analysis is not possible simply because the quantity of water on the pyrite surface is much too small to either collect or analyze.

The closest approach to direct analysis of the ferric/ferrous ratio at the pyrite surface is obtained by washing the surface of a pyritic sample (an exposed coal face for example) with dilute acid and analyzing the wash water. The ferric/ferrous ratio obtained thereby could be much higher and in no case will be less than that ratio which exists in solution at the reaction site, for the following reasons: the majority of the salts collected in the wash will originate from solutions which are not in contact with the surface of pyrite. Even insignificant microbial activity--that is, insignificant in relation to oxygenation of pyrite--could raise the ferric/ferrous ratio in these solutions not in contact

with pyrite to very high levels. But these solutions have little effect on the overall pyrite oxidation rate for three reasons: 1) there is little solution and therefore few ferric ions involved, 2) according to the stoichiometry, 14 mole of ferric ions are required to oxidize one mole of pyrite (FeS_2), and 3) the diffusion rate of these solutions is very slow so that the rate at which solutions of high ferric/ferrous ratios move to the pyrite surfaces is low.

Three different sections of coal in Auger Hole No. 2B were washed with distilled water and the washings collected. The ferric/ferrous ratios of the washings were 0.10, 0.43, and 0.28 (9.4, 30, and 22 percent ferric iron). The section having the highest pyritic sulfur content had the lowest (0.10) ferric/ferrous ratio, while the higher ferric/ferrous ratios were found in the washings from the coal section having low pyrite concentration. This is to be expected since coal of higher pyrite content will have a greater percentage of its adsorbed water in contact with a pyrite surface.

The only real "evidence" based on field observations, to support the widely held premise that bacteria have a major role in the formation of acid drainage is that the effluent from many underground mines has a high concentration of Ferrobaccillus ferrooxidans and a high ferric/ferrous ratio. Obviously bacteria are active or the ferrous ions would not be oxidized to ferric at the low pH's found. For example, the discharge from McDaniels mine when under 10 to 20 percent oxygen has a ferric/ferrous ratio of 10/1 to 20/1 (90 to 95 percent ferric).

However, as pointed out before, the effluent water is in no way representative of the water in contact with reaction sites. Another important point should be made: the bacterially enhanced ferrous-to-ferric oxidation reaction occurs in the aqueous solution, not on the pyrite surface (see Reference 6). With these points in mind, the role of bacteria and their influence on discharge water from McDaniels mine and auger holes can be explained.

Let us first state that the high ferric-ferrous ratio observed in the discharge from McDaniels mine and the auger holes is generated after contact with pyritic material, and then prove the validity of this statement by examining data obtained.

According to Smith and Shumate (6), if the ferric-ferrous ratio of a solution in contact with pyritic material is less than 0.3 (24 percent ferric) the oxygenation rate in air is five times greater than the ferric ion oxidation rate. At a ferric/ferrous ratio of 2.2 (70 percent ferric) the oxygenation and ferric ion oxidation rate are approximately equal. The important question to be answered is where the water of high ferric/ferrous ratios is found. If ferric/ferrous ratios above 0.3 are generated after the water passes through the pyritic material these waters do not have a significant effect on the rate of pyrite oxidation or therefore on acid discharge. Data described below indicate that the high ferric/ferrous ratios observed in effluent water from McDaniels mine and

the auger holes is generated in water ponded on the clay floor, out of contact of pyritic material, and that the water coming through the working face of the mine into the ponded area has a ferric/ferrous ratio under 0.25 (20 percent ferric).

The ferric/ferrous ratios of the auger hole discharges increase with longer residence time in the holes. For example, water flowing from Hole No. 6, before weekly pumping was started, had a ferric/ferrous ratio varying from 3.0 to 9.0. Average residence time of water without pumping was approximately a month. When weekly pumping operations were started, the ferric/ferrous ratio dropped to 0.25 (20 percent ferric).

When other auger holes were pumped, the water that flowed into the hole immediately after the hole was pumped down had a ferric/ferrous ratio under 0.3, even when the pumped water had a ratio over 5.0.

These data show that the major increase in ferric-ferrous ratio occurs in the ponded water and that the ferric/ferrous ratio of water entering the ponds is relatively low. Data obtained from McDaniels mine after nitrogen was added and the oxygen concentration was reduced to less than 1 percent indicate that the ferric/ferrous ratio of water behind the working face, on the reaction sites, has a low ferric/ferrous ratio. As noted above, the effluent from McDaniels when the mine was open to air had a ferric/ferrous ratio above 10. When oxygen dropped below 1 percent, the ferric/ferrous ratio dropped below 0.1 (10 percent ferric) immediately. The salts appearing in the effluent when the mine is under nitrogen were formed during the previous period when the oxygen concentration was 21 percent. The ferric/ferrous ratio of these products was determined by the condition prevailing when formed. While some reduction of ferric ions is likely when solutions are transported over pyrite to reach the effluent water, reduction to less than 10 percent ferric is very unlikely if the initial ferric-ferrous ratio were over 0.25 (20 percent ferric). From these data it would appear that the ferric/ferrous ratio of solutions behind the working face have ferric/ferrous ratios around 0.1 or 0.15.

Other analyses of the underground pyritic system will lead to the same conclusion--ferric/ferrous ratios of water at the majority of reaction sites are too low to make ferric ion oxidation significant. The steady-state ferric/ferrous ratio reached in a solution in contact with pyrite will depend on the relative rates of two reactions: 1) rate of ferric ion generation by microbial oxidation of ferrous ions and 2) the rate of ferric ion reduction by reaction with pyrite. Increasing the number or activity of bacteria relative to the surface area of pyrite exposed to the solution will increase the ferric/ferrous ratio. That is, if a relatively constant concentration and activity of bacteria are assumed per unit volume of solution, then the greater the volume of water per unit surface area of exposed pyrite, the higher the ferric/ferrous ratio in solution will be. Also, the closer the solution is to a pyrite surface, the lower the ferric/ferrous ratio will be up to the point where ferric ions are so close to the pyritic that no resistance to mass transfer is present. In other words, solutions in direct contact with a pyritic surface have the lowest ferric/ferrous ratio. As solutions become more dilute and further removed from contact with pyrite, ferric/ferrous ratios increase.

Let us trace the path of water in contact with a reaction site. Regardless of its location the water (solution) will tend to diffuse and "weep" downward under the influence of gravity. As the solution adsorbs moisture from the air the volume increases and the solution moves away from the pyrite surface. The ferric/ferrous ratio will increase if any microbiological activity is present. Additional contact with pyritic material may be made, but increased volume of solution will reduce contact time so that the overall or general trend will be an increase in ferric-ferrous ratio with movement toward the flow channels. Once the solution does reach the point where it is either removed by percolation or flushing, dilution as well as pH would increase, allowing further increase in the ferric/ferrous ratio of the water with which we started. This shows that the ferric-ferrous ratio of water entering the effluent stream of a mine has, on the average, the highest ferric/ferrous ratio to be found in water which contacted pyritic material on its way to the discharge stream.

Experimental data have shown that water behind the working face of a mine has a low ferric/ferrous ratio (0.25 or 20 percent ferric or lower). At such ferric/ferrous ratios, microbial induced oxidation is small compared to oxygenation. Therefore acid mine drainage produced as the result of microbial activity is small compared to that produced by oxygenation, which is independent of microbial activity.

Discussion of Future Work

One of the general objectives of this and future work at the McDaniels research complex is to develop a fundamental understanding of the kinetics of mine drainage in underground pyritic systems. This encompasses both the kinetics of formation (i.e. pyrite oxidation) and the removal or transport of pyrite oxidation products to the receiving stream.

The basic kinetics of formation have been determined in a laboratory. The application of these basic data require a knowledge of the range of environmental conditions which exist at reaction sites in a natural system. A quantitative model of a natural system requires that the relative number of reaction sites exposed to a given set of environmental conditions be known. A model, based on the hydrologic and geologic features of the area under study, can be quantified only on the basis of meaningful field data.

Field data are equally important to evaluating removal mechanisms and their kinetics. One of the major unknowns in underground pyritic systems is the relative importance of the different product transport mechanisms. Here again, the only logical procedure to use in evaluating these mechanisms is interpretation of data from real systems.

To be useful, field data must be capable of precise interpretation. The following example may be used to illustrate the importance of good data. Following the change in acid load caused by decreasing oxygen concentration to zero is one method of evaluating removal mechanisms. Without

the formation of oxidation products, acid load due to diffusion and "flushing" mechanisms (after peak flow) drop to zero, while the load due to percolation would stay approximately the same for at least six months to a year (since the percolate is a saturated solution). Only a 30 to 40 percent change in acid load occurs during the first year after oxygen concentration is dropped to zero. Hydrologic variations from one year to the next may cause a similar change in acid load. Therefore, in order to determine the change in acid load due to change in oxygen, some way of separating the effect of hydrologic conditions and oxygen composition is necessary. The multiple mine facility provides the means of determining change in acid load due only to hydrologic variation since the only variable examined in the reference mine is the hydrologic conditions. There is no other type of experimental facility capable of providing data in a reasonable period of time that may be interpreted with the precision required to determine mine drainage kinetics of underground pyritic systems.

ACKNOWLEDGMENTS

The authors, Professors Edwin E. Smith, Department of Chemical Engineering, and K. S. Shumate, Department of Civil Engineering appreciate the help given by the many students and faculty who have assisted in the development of the McDaniels research complex.

The valuable assistance of part-time student employees, who spent many long Saturdays in all kinds of weather "at the mines" is sincerely appreciated. We are particularly indebted to James Wood, Mark McLaughlin, William Syverson, and Michael Neibler for their reliable support.

Much of the analytical work was ably performed by or under the direction of Mr. Paul Smith, Research Associate, Engineering Experiment Station.

The financial support of the Federal Water Quality Administration through Contract 14-12-97 (program #14010 EXA) and the help provided by Mr. Ronald D. Hill, project officer, is gratefully acknowledged.

Preceding page blank

REFERENCES

1. Hillebrand, Lundell, Bright, Heffman, "Applied Inorganic Analysis," 2nd Edition, J. Wiley & Sons, Inc., New York (1953).

2. Lau, C. M., Shumate, K. S., Smith, E. E., "The Role of Bacteria in Pyrite Oxidation Kinetics," Third Symposium of Coal Mine Drainage, Mellon Institute.

3. Scott, W. W., "Standard Methods of Chemical Analysis," 5th Edition, Vol. I, p. 908, D. Van Nostrand Co., Inc., New York (1939).

4. Shumate, K. S., Smith, E. E., Brant, R. A., "A Model for Pyritic Systems," ACS Division of Fuel Chemistry Symposium, Preprints, 157th National Meeting 13, No. 2 (1969).

5. Shumate, K. S., Smith, E. E., "Development of a Natural Laboratory for the Study of Acid Mine Drainage Production," Second Symposium on Coal Mine Drainage, Preprints, Mellon Institute, Pittsburgh, Pa., (May, 1968).

6. Smith, E. E., Shumate, K. S., "Sulfide-to-Sulfate Reaction Mechanism," Water Pollution Control Research Services, 14010 FPS 02/70 (1970).

7. Smith, E. E., Shumate, K. S., "Development of a Natural Laboratory for the Study of Acid Mine Drainage Production," Final Report, U. S. Department of Interior (1968).

LIST OF PUBLICATIONS

Shumate, K. S., Smith, E. E., "Development of a Natural Laboratory for the Study of Acid Mine Drainage Production," Second Symposium on Coal Mine Drainage, Preprints, Mellon Institute, Pittsburgh, Pa., May 14-15, 1968.

Shumate, K. S., Smith, E. E., Brant, R. A., "A Model for Pyritic Systems," ACS Division of Fuel Chem. Symposium, Preprints, 157the National Meeting 13, No. 2, (1969).

Preceding page blank

GLOSSARY

ACID (AND SULFATE) LOAD

Rate of acid (or sulfate) discharged in units of pounds per day. Acidity expressed in pounds of equivalent $CaCO_3$.

FERRIC ION OXIDATION

One of the two basic modes of pyrite oxidation. The other mode is "oxygenation." Ferric ion oxidation occurs when a ferric ion is adsorbed on a pyrite surface, accepts an electron from the pyrite and is thereby reduced to the ferrous state. Ferric ions are the immediate oxidizing agent. When oxygen is adsorbed and becomes the immediate electron acceptor, the oxidation mode is termed oxygenation.

OXYGENATION

(see Ferric Ion Oxidation)

REACTION SITE

Surface of pyrite exposed to oxygen in which the oxygen may be present as dissolved (inaqueous solution) oxygen or in a humid atmosphere.

RESPONSE TIME

(For the type of analysis used in this report) Time that a system requires to reach (e.g. 90% of) steady-state after a step change in operating conditions.

SULFATE LOAD

(see Acid Load)

VAPOR PHASE OXIDATION

Oxidation which occurs when the reaction site is exposed to a continuous vapor phase so that the transport of oxygen is through a gaseous rather than liquid or solid phase. This does not imply the absence of liquid water which is always present as adsorbed water in a natural system.

Preceding page blank

APPENDIX I

DISCHARGE DATA

Table VII

1965 MCDANIELS MINE DATA

DATE		FLOW, GPD	ACID, PPM
AUG	17	324.0	65.0
AUG	19	312.0	65.0
AUG	24	292.0	55.0
AUG	25	274.0	55.0
AUG	26	295.0	55.0
AUG	31	292.0	59.0
SEPT	1	292.0	70.0
SEPT	2	277.0	70.0
SEPT	7	284.0	59.0
SEPT	8	287.0	64.0
SEPT	9	286.0	60.0
SEPT	15	307.0	73.0
SEPT	16	290.0	78.0
SEPT	21	293.0	73.0
SEPT	23	295.0	77.0
OCT	9	293.0	82.0
OCT	15	278.0	71.0
OCT	23	307.0	100.0
OCT	30	283.0	77.0
NOV	6	284.0	89.0
NOV	13	290.0	92.0
NOV	20	296.0	98.0
DEC	4	295.0	122.0
DEC	11	289.0	116.0
DEC	18	283.0	130.0
DEC	21	271.0	119.0
DEC	29	281.0	137.0

Preceding page blank

Table VII (continued)

1966 MCDANIELS MINE DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM
JAN 8	296.0	183.0	
JAN 15	313.0	153.0	
JAN 22	312.0	123.0	
FEB 12	293.0	204.0	
FEB 26	354.0	155.0	
MAR 5	395.0	189.0	
MAR 12	354.0	146.0	
MAR 18	365.0	177.0	
MAR 25	339.0	147.0	
APR 2	337.0	142.0	
APR 9	331.0	147.0	
APR 16	374.0	132.0	
APR 23	354.0	152.0	
APR 30	454.0	163.0	
MAY 7	512.0	154.0	
MAY 14	454.0	137.0	
MAY 21	442.0	143.0	
MAY 27	441.0	150.0	
JUNE 4	378.0	121.0	
JUNE 11	318.0	105.0	
JUNE 15	312.0	106.0	
JUNE 25	286.0	122.0	
JUNE 29	334.0	104.0	
JULY 8	254.0	119.0	
JULY 14	318.0	141.0	
JULY 21	316.0	102.0	
AUG 6	263.0	94.0	
AUG 11	258.0	98.0	
AUG 26	246.0	100.0	
SEPT 2	237.0	82.0	
SEPT 16	223.0	81.0	
SEPT 30	243.0	75.0	
OCT 6	206.0	74.0	
OCT 8	208.0	75.0	
OCT 12	208.0	76.0	
OCT 15	210.0	77.0	
OCT 18	210.0	85.0	
OCT 21	206.0	79.0	
OCT 29	202.0	71.0	
NOV 5	195.0	78.0	
NOV 12	199.0	112.0	
NOV 19	196.0	76.0	
NOV 26	201.0	72.0	
DEC 3	187.0	92.0	
DEC 10	199.0	142.0	
DEC 17	201.0	89.0	
DEC 23	196.0	70.0	
DEC 31	199.0	62.0	

Table VII (continued)

1967 MCDANIELS MINE DATA

DATE	FLOW, GPD	ACID, PPM	SO4, PPM
JAN 7	211.0	75.0	
JAN 14	214.0	80.0	
JAN 21	207.0	60.0	
MAR 25	342.0	128.0	
APR 1	339.0	212.0	
APR 8	375.0	124.0	
APR 15	404.0	112.0	
APR 22	398.0	132.0	
APR 29	368.0	84.0	
MAY 6	377.0	102.0	
MAY 13	485.0	108.0	
MAY 20	502.0	96.0	
MAY 27	477.0	76.0	
JUNE 3	503.0	70.0	
JUNE 10	444.0	55.0	
JUNE 14	404.0	60.0	
JUNE 16	400.0	56.0	
JUNE 20	368.0	68.0	
JUNE 24	334.0	58.0	
JUNE 27	318.0	62.0	
JULY 1	306.0	54.0	
JULY 8	274.0	58.0	
JULY 13	266.0	44.0	
JULY 15	249.0	58.0	
JULY 20	240.0	50.0	
AUG. 10	202.0	32.0	
AUG 12	196.0	42.0	
AUG 19	199.0	34.0	
AUG 23	198.0	50.0	
AUG 26	195.0	34.0	
SEPT 2	192.0	42.0	
SEPT 9	192.0	40.0	
SEPT 16	188.0	46.0	
SEPT 23	187.0	53.0	
OCT 1	184.0	55.0	
OCT 11	184.0	72.0	
OCT 14	187.0	70.0	
OCT 21	194.0	76.0	
OCT 28	185.0	86.0	
NOV 4	185.0	98.0	
NOV 11	182.0	86.0	
NOV 18	188.0	82.0	
NOV 25	184.0	100.0	
DEC 2	181.0	94.0	
DEC 9	175.0	88.0	
DEC 16	184.0	92.0	
DEC 23	182.0	86.0	

Table VII (continued)

1968 MCDANIELS MINE DATA

DATE		FLOW,GPD	ACID,PPM	SO4,PPM
JAN	6	230.0	85.0	
JAN	20	237.0	88.0	
JAN	27	288.0	95.0	
FEB	3	275.0	270.0	
FEB	10	177.0	140.0	
FEB	17	195.0	146.0	
FEB	24	195.0	196.0	
MAR	2	189.0	114.0	
MAR	9	194.0	106.0	
MAR	16	240.0	246.0	
MAR	25	254.0	200.0	
MAR	28	405.0	248.0	
APR	6	345.0	280.0	
APR	9	345.0	268.0	
APR	13	300.0	284.0	
APR	27	390.0	318.0	
MAY	4	330.0	260.0	
MAY	11	345.0	285.0	
MAY	18	495.0	325.0	
MAY	25	675.0	231.0	
MAY	27	788.0	316.0	
JUNE	1	600.0	245.0	
JUNE	6	455.0	203.0	
JUNE	14	300.0	130.0	
JUNE	18	188.0	225.0	
JUNE	28	293.0	181.0	
JULY	1	248.0	173.0	
JULY	5	293.0	136.0	
JULY	19	315.0	186.0	
JULY	26	270.0	181.0	
AUG	2	293.0	171.0	
AUG	9	234.0	161.0	
AUG	23	263.0	150.0	
SEPT	10	248.0	115.0	
SEPT	13	234.0	142.0	
SEPT	17	232.0	136.0	

Table VII (continued)

1968 MCDANIELS MINE DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM
SEPT 20	240.0	115.0	
SEPT 24	221.0	118.0	
OCT 8	213.0	112.0	
OCT 12	220.0	116.0	
OCT 19	198.0	110.0	
OCT 26	198.0	95.0	176.0
OCT 29	179.0	105.0	178.0
NOV 2	160.0	97.0	
NOV 5	149.0	90.0	
NOV 9	198.0	125.0	
NOV 12	198.0	100.0	
NOV 16	198.0	100.0	
NOV 19	202.0	92.5	
NOV 23	202.0	97.5	
NOV 26	190.0	97.0	
NOV 30	205.0	82.0	
DEC 5	198.0	97.0	167.0
DEC 7	200.0	97.0	179.0
DEC 10	200.0	95.0	
DEC 17	198.0	100.0	
DEC 20	207.0	95.0	
DEC 23	204.0	125.0	
DEC 28	224.0	140.0	
DEC 31	207.0	95.0	

Table VII (continued)

1969 MCDANIELS MINE DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM
JAN 4	207.0	137.0	
JAN 11	212.0	204.0	
JAN 18	182.0	92.0	172.0
JAN 25	231.0	157.0	242.0
JAN 28	251.0	135.0	225.0
FEB 1	289.0	235.0	324.0
FEB 8	274.0	265.0	335.0
FEB 15	274.0	195.0	276.0
FEB 22	243.0	155.0	245.0
FEB 25	224.0	182.0	274.0
MAR 1	224.0	145.0	240.0
MAR 8	224.0	145.0	234.0
MAR 15	194.0	135.0	226.0
MAR 22	176.0	140.0	234.0
MAR 29	285.0	280.0	360.0
APR 5	326.0	240.0	332.0
APR 8	327.0	270.0	359.0
APR 12	319.0	260.0	343.0
APR 22	440.0	260.0	350.0
APR 26	411.0	232.0	331.0
MAY 3	356.0	212.0	298.0
MAY 6	334.0	195.0	292.0
MAY 10	422.0	282.0	382.0
MAY 13	497.0	235.0	322.0
MAY 17	378.0	187.0	286.0
MAY 24	347.0	179.0	243.0
MAY 20	365.0	197.0	288.0
MAY 31	0.0	173.0	305.0
JUNE 6	319.0	150.0	239.0
JUNE 9	296.0	140.0	237.0
JUNE 12	294.0	135.0	224.0
JUNE 21	315.0	127.0	227.0
JUNE 26	282.0	125.0	212.0
JULY 3	274.0	110.0	206.0
JULY 17	226.0	102.0	198.0
JULY 24	231.0	107.0	186.0

Table VII (continued)

1969 MCDANIELS MINE DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM	PH
JULY 28	266.0	97.0	191.0	
JULY 30	260.0	95.0	183.0	
AUG 8	240.0	77.0	209.0	
AUG 15	236.0	87.0	178.0	
AUG 20	260.0	95.0	182.0	
AUG 27	205.0	82.0	164.0	
SEPT 3	185.0	72.0	155.0	
SEPT 17	193.0	67.0	155.0	
SEPT 25	193.0	65.0	148.0	
OCT 4	176.0	72.0	148.0	
OCT 11	176.0	67.0	148.0	
OCT 18	160.0	100.0	148.0	
OCT 25	220.0	67.0	141.0	
NOV 1	213.0	62.0	143.0	
NOV 8	180.0	60.0	137.0	
NOV 22	182.0	57.0	134.0	
NOV 29	160.0	62.0	138.0	3.2
DEC 6	180.0	65.0	133.0	3.4
DEC 20	180.0	55.0	139.0	3.2

Table VII (continued)

1970 MCDANIELS MINE DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM	PH
JAN 3	188.0	60.0	137.0	3.25
JAN 17	180.0	55.0	129.0	3.2
JAN 24	160.0	57.0	133.0	3.2
JAN 31	213.0	95.0	174.0	3.0
FEB 7	225.0	92.0	174.0	2.95
FEB 14	235.0	100.0	173.0	2.9
FEB 21	210.0	105.0	175.0	2.85
FEB 28	202.0	82.0	151.0	3.05
MAR 7	282.0	117.0	193.0	2.94
MAR 14	274.0	107.0	181.0	2.95
MAR 21	290.0	135.0	210.0	2.9
MAR 27	310.0	110.0	190.0	2.9
APR 4	260.0	145.0	220.0	2.9
APR 11	255.0	140.0	216.0	3.15
APR 18	285.0	132.0	205.0	3.45
APR 25	418.0	175.0	250.0	3.3
MAY 2	430.0	157.0	220.0	3.25
MAY 16	400.0	155.0	207.0	3.5
MAY 23	365.0	142.0	211.0	3.25
MAY 30	420.0	135.0	196.0	3.35
JUNE 6	365.0	105.0	180.0	3.0
JUNE 13	330.0	105.0	183.0	3.45
JUNE 17	285.0	105.0	185.0	3.45
JUNE 26	320.0	83.0	199.0	3.4
JULY 1	242.0	87.0	169.0	3.4
JULY 7	272.0	90.0	165.0	3.5
JULY 13	272.0	75.0	142.0	3.75
JULY 17	242.0	80.0	155.0	3.35
JULY 22	242.0	85.0	158.0	3.7
JULY 24	270.0	75.0	154.0	3.2
JULY 29	234.0	75.0	154.0	3.8
AUG 1	270.0	80.0	153.0	3.35
AUG 6	250.0	87.0	154.0	3.85
AUG 12	258.0	92.0	160.0	3.95
AUG 19	251.0	75.0	154.0	3.9
AUG 26	219.0	65.0	151.0	3.68
SEPT 2	231.0	67.0	144.0	3.8
SEPT 10	250.0	77.0	145.0	4.0
SEPT 16	243.0	67.0	138.0	4.22
SEPT 29	243.0	80.0	128.0	3.72
OCT 5	220.0	55.0	124.0	3.68

Table VIII

1969 AUGER HOLE 1 DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM	PH
JULY 30	123.0	250.0	568.0	2.75
AUG 4	270.0	250.0	645.0	2.72
AUG 8	87.0	162.0	557.0	3.0
AUG 15	114.0	187.0	501.0	2.7
AUG 20	100.0	245.0	572.0	2.7
AUG 27	76.0	160.0	475.0	2.83
SEPT 3	66.0	242.0	591.0	2.8
SEPT 10	60.0	265.0	637.0	2.7
SEPT 18	52.0	205.0	562.0	2.7
SEPT 25	58.0	222.0	587.0	2.5
OCT 11	68.0	185.0	507.0	2.8
OCT 25	61.0	100.0	437.0	3.15
NOV 7	61.0	102.0	426.0	2.95
NOV 8	75.0	105.0	426.0	2.95
NOV 22	114.0	65.0	386.0	3.45
NOV 29	81.0	60.0	386.0	3.45
DEC 6	175.0	65.0	381.0	3.4
DEC 20	111.0	75.0	362.0	3.05

1970 AUGER HOLE 1 DATA

JAN 3	167.0	110.0	424.0	3.0
JAN 17	165.0	42.0	339.0	3.4
JAN 31	251.0	200.0	493.0	2.65
FEB 7	215.0	105.0	378.0	2.8
FEB 14	213.0	140.0	404.0	2.8
FEB 21	195.0	100.0	358.0	2.85
FEB 28	148.0	60.0	310.0	2.85
MAR 7	342.0	152.0	370.0	2.87
MAR 14	365.0	145.0	355.0	2.87
MAR 21	367.0	190.0	404.0	2.8
MAR 28	324.0	115.0	332.0	3.0
APR 4	385.0	145.0	351.0	2.85
APR 11	245.0	100.0	323.0	2.95
APR 18	240.0	117.0	343.0	3.0
APR 25	470.0	162.0	320.0	2.9
MAY 2	290.0	217.0	424.0	2.85
MAY 16	405.0	237.0	434.0	3.2
MAY 23	202.0	177.0	382.0	2.85
MAY 30	230.0	160.0	355.0	2.85

Table VIII (continued)

1970 AUGER HOLE 1 DATA

DATE	FLOW,GPD	ACID,PPM	SO4,PPM	PH
JUNE 6	137.0	180.0	403.0	2.75
JUNE 13	105.0	237.0	486.0	2.75
JUNE 26	92.0	208.0	515.0	2.9
JULY 1	104.0	390.0	670.0	2.7
JULY 7	100.0	255.0	534.0	2.65
JULY 13	106.0	252.0	467.0	2.75
JULY 17	98.0	270.0	563.0	2.75
JULY 22	88.0	242.0	517.0	2.8
AUG 6	106.0	265.0	533.0	2.8
AUG 12	182.0	322.0	584.0	2.75
AUG 19	106.0	210.0	468.0	2.8
SEPT 2	61.0	195.0	473.0	2.8
SEPT 10	107.0	230.0	509.0	2.9
SEPT 16	107.0	230.0	525.0	2.75
SEPT 29	122.0	195.0	456.0	3.00
OCT 5	64.0	140.0	403.0	3.02

Table IX

1969 AUGER HOLE 2A DATA

DATE	FLOW, GPD	ACID, PPM	SO4, PPM	PH
JULY 30		1675.0	2484.0	2.61
AUG 4	30.2	1191.0	2055.0	2.65
AUG 8	8.2	962.0	2011.0	2.71
AUG 15	4.2	840.0	1620.0	2.50
AUG 20	2.2	932.0	1687.0	2.56
AUG 27	4.2	995.0	1637.0	2.60
SEPT 3	2.4	787.0	1647.0	2.70
SEPT 10	4.8	797.0	1701.0	2.7
SEPT 17	1.1			
SEPT 17	1.1	500.0	1537.0	2.9
SEPT 25	1.0	22.0	537.0	2.5
OCT 4	1.0		1435.0	
OCT 11	1.6	490.0	1353.0	2.75
OCT 18	2.8	512.0	1313.0	2.8
OCY 25	2.0	350.0	1031.0	2.9
NOV 1	2.0	430.0	1255.0	2.85
NOV 8	2.2	325.0	964.0	2.9
NOV 22	0.5	227.0	692.0	3.1
NOV 29	2.0	305.0	917.0	3.1
DEC 6	2.5	302.0	940.0	3.1
DEC 20	6.0	482.0		2.8

1970 AUGER HOLE 2A DATA

JAN 30	9.6	1510.0	1996.0	2.6
JAN 17	10.6	1155.0	1841.0	2.5
JAN 24	12.0	1082.0	1690.0	2.55
JAN 31	28.0	1110.0	1600.0	2.4
FEB 7	19.4	1435.0	1906.0	2.3
FEB 14	28.0	1662.0	2010.0	2.25
FEB 21	25.0	1890.0	2282.0	2.25
FEB 28	21.6	1355.0	1679.0	2.4
MAR 7	31.0	1660.0	1981.0	2.55
MAR 14	47.0	1442.0	1778.0	2.50
MAR 21	35.0	1617.0	1949.0	2.4
MAR 28	35.0	1520.0	1786.0	2.4
APR 11	30.0	1972.0	2185.0	2.45
APR 18	33.0	1240.0	1524.0	2.6
APR 25		1367.0	1643.0	2.5
MAY 16		662.0	793.0	2.85
MAY 23		1300.0	1526.0	2.5
MAY 30	44.0	1005.0	1278.0	2.45
JUNE 13	14.0	910.0	1236.0	2.5
JUNE 17	13.0	895.0	1260.0	2.7
JUNE 26	3.0	1115.0	1505.0	2.7
JULY 1	14.0	837.0	1172.0	2.6
JULY 7	12.0	1017.0	1478.0	2.5
JULY 17	7.0	790.0	1180.0	2.6
AUG 12	12.0	1665.0	2108.0	2.55
AUG 19	10.0	1165.0	1555.0	2.55
SEPT 2	7.0	1222.0	1698.0	2.65
SEPT 16	4.2	980.0	1480.0	2.6
SEPT 29	847.0	995.0	2.8	

Table X

1969 AUGER HOLE 28 DATA

DATE	FLOW, GPD	ACID, PPM	SO4, PPM	PH
OCT 4	10.6	15.0	252.0	
SEPT 25	9.6	22.0	255.0	4.
AUG 4	40.1	68.0	331.0	3.14
AUG 8	21.1	50.0	306.0	3.71
AUG 20	24.3	60.0	266.0	3.27
AUG 27	19.9	45.0	246.0	3.42
SEPT 3	15.0	42.0	263.0	3.6
SEPT 10	12.5	62.0	360.0	3.4
SEPT 17	9.9	47.0	313.0	3.7
OCT 11	18.5	27.0	271.0	3.8
OCT 18	37.0	242.0		4.0
OCT 25	9.2	30.0	299.0	4.05
NOV 1	9.6	7.0	227.0	5.1
NOV 8	33.5	105.0	363.0	3.05
NOV 22	26.0	115.0	308.0	2.95
NOV 29	35.0	50.0	227.0	3.5
DEC 6	13.1	30.0	207.0	3.8
DEC 20	72.1	152.0	361.0	2.9

1970 AUGER HOLE 28 DATA

JAN 3	60.6	120.0	300.0	3.0
JAN 17	63.0	175.0	224.0	3.3
JAN 24	86.0	52.0	213.0	3.35
JAN 31	130.0	130.0	309.0	2.3
FEB 7	135. +	55.	250.	3.2
FEB 14	128. +	30.	144.	2.4
FEB 21	130. +	50.	169.	3.2
FEB 28	130.0	40.0	156.0	3.8
MAR 7	184. +	52.	168.	3.23
MAR 14	302. +	27.	135.	3.6
MAR 21	OVERFLOW	25. #	128. #	3.6
MAR 28	OVERFLOW	32. #	136. #	3.4
APR 4	OVERFLOW	50. #	131. #	3.2
APR 11	OVERFLOW	12. #	86. #	3.9
APR 18	OVERFLOW	17. #	103. #	3.9
APR 25	OVERFLOW	20. #	103. #	3.8
MAY 30	220.0	17.0	100.0	3.7
JUNE 6	105.0	35.0	125.0	3.4
JUNE 13	51.0	42.0	160.0	3.45
JUNE 17	125.0	57.0	184.0	3.2
JUNE 26	52.0	196.0	204.0	3.4
JULY 1	44.0	57.0	171.0	3.4
JULY 11	51.0	52.0	137.0	3.3
JULY 17	66.0	150.0	232.0	2.9
AUG 12	182.0	200.0	307.0	2.8
AUG 19	98.0	115.0	237.0	2.95
SEPT 2	40.0	85.0	210.0	3.2
SEPT 16	22.4	62.0	202.0	3.3
SEPT 29	29.6	100.0	258.0	3.2

OVERFLOW VALUES WERE CALCULATED FROM AVERAGE
MISSED VALUES

Table XI

1969 AUGER HOLE 3 DATA

DATE	FLOW, GPD	ACID, PPM	SO4, PPM	PH
AUG 4	43.0	17.0	428.0	3.85
AUG 8	59.3	5.0	439.0	3.65
AUG 15	47.0	5.0	325.0	5.6
AUG 20	42.7	5.0	327.0	5.42
AUG 27	38.6	2.0	282.0	6.10
SEPT 3	35.3		300.0	6.0
SEPT 10	31.2	73.(ALK)	252.0	
SEPT 17	29.5	37.(ALK)	256.0	
SEPT 25	27.6	52.(ALK)	281.0	
OCT 4	26.7	30.(ALK)	285.0	
OCT 11	27.0	2.0	312.0	5.7
OCT 18	28.1	32.0	304.0	5.8
OCT 25	23.9	40.(ALK)	311.0	
NOV 1	25.0	42.(ALK)	295.0	
NOV 8	27.0	36.(ALK)	288.0	
NOV 22	29.0	5.0	294.0	5.9
NOV 29	29.0	6.(ALK)	282.0	
DEC 6	30.0	43.(ALK)	272.0	
DEC 20	37.0	7.0	329.0	5.6

1970 AUGER HOLE 3 DATA

JAN 17	62.0	175.0	715.0	2.9
JAN 24	47.5	57.0	500.0	3.4
JAN 31	116.0	530.0	1240.0	2.5
FEB 7	181.0	835.0	1228.0	2.4
FEB 14	153.0	827.0	1096.0	2.35
FEB 21	279.0	405.0	673.0	2.48
FEB 28	133.0	245.0	527.0	2.67
MAR 7	212.0	392.0	611.0	2.67
MAR 14	236.0	245.0	427.0	3.1
MAR 21	322.0	297.0	483.0	2.7
MAR 28	335.0	287.0	441.0	2.7
APR 11	323.0	277.0	448.0	2.7
APR 18	128.0	170.0	315.0	3.0
APR 25	565.0	177.0	285.0	2.9
MAY 30	450.0	172.0	290.0	2.8
JUNE 6	165.0	150.0	327.0	2.9
JUNE 17	85.0	90.0	294.0	3.3
JULY 1	75.0	65.0	267.0	3.35
JULY 22	63.0	77.0	477.0	3.35
AUG 12	97.0	270.0	491.0	2.8
AUG 19	120.0	272.0	538.0	2.75
AUG 26	65.0	170.0	407.0	3.0
SEPT 10	49.0	75.0	319.0	3.6
SEPT 16	37.4	97.0	360.0	3.4

Table XII

1969 AUGER HOLE 4 DATA

DATE -	FLOW,GPD	ACID,PPM	SO4,PPM	PH
AUG 4	40.1	2.0	333.0	5.24
AUG 8	36.5	14.0	531.0	4.62
AUG 15	36.7	5.0	399.0	5.6
AUG 20	39.1	62.(ALK)	373.0	
AUG 27	35.3	17.0	604.0	4.40
SEPT 3	31.5	5.0	334.0	6.3
SEPT 10	29.8	0.(ALK)	423.0	
SEPT 17	27.7	55.(ALK)	346.0	
SEPT 25	26.3	60.(ALK)	371.0	
OCT 4	26.2	7.0	313.0	6.1
OCT 11	27.0	60.(ALK)	405.0	
OCT 18	27.5	10.0	334.0	6.4
OCT 25	26.9	77.(ALK)	360.0	
NOV 1	25.8	57.(ALK)	331.0	
NOV 8	27.5	50.(ALK)	324.0	
NOV 22	29.0	2.(ALK)	492.0	
NOV 29	33.0	10.(ALK)	339.0	
DEC 6	31.6	70.(ALK)	323.0	
DEC 20	30.7	60.(ALK)	423.0	

1970 AUGER HOLE 4 DATA

JAN 3	43.3	107.0	898.0	3.5
JAN 17	44.5	120.0	977.0	3.5
JAN 24	39.0	10.0	527.0	5.5
JAN 31	168.0	325.0	786.0	2.65
FEB 7	173.0	435.0	1022.0	2.6
FEB 14	270.0	360.0	640.0	2.6
FEB 21	91.0	305.0	770.0	2.6
FEB 28	68.0	220.0	670.0	2.83
MAR 7	193.0	192.0	445.0	2.83
MAR 14	170.0	222.0	504.0	2.9
MAR 21	228.0	205.0	419.0	3.0
MAR 28	217.0	245.0	482.0	2.7
APR 4	471.0	132.0	272.0	2.85
APR 11	202.0	265.0	538.0	2.75
APR 18	140.0	235.0	617.0	2.95
JUNE 6	237.0	75.0	459.0	2.9
JUNE 13	98.0	122.0	540.0	3.2
JUNE 17	78.0	120.0	588.0	3.3
JULY 1	45.0	65.0	407.0	3.65
JULY 7	51.0	100.0	485.0	3.35
JULY 17	36.0	85.0	537.0	3.3
AUG 12	96.0	152.0	453.0	3.05
SEPT 2	65.0	215.0	662.0	3.0
SEPT 10	41.0	182.0	453.0	3.5
SEPT 16	35.4	72.0	430.0	3.55

Table XIII

1969 AUGER HOLE 5 DATA

DATE	FLOW, GPD	ACID, PPM	SO4, PPM	PH
AUG 4	26.9	3.0	388.0	5.75
AUG 8	25.9	53.0	524.0	3.39
AUG 15	25.2	55.0	459.0	3.4
AUG 20	25.9	85.0	398.0	3.10
AUG 27	25.2	35.0	364.0	3.52
SPET 3	30.9	42.0	440.0	3.4
SEPT 10	20.2	87.0	476.0	3.1
SEPT 17	20.2	137.0	632.0	2.9
SEPT 25	18.8	100.0	497.0	2.9
OCT 4	18.8	125.0	516.0	2.9
OCT 11	19.2	122.0	513.0	2.9
OCT 18	19.7	125.0	413.0	3.1
OCT 25	18.2	150.0	617.0	2.95
NOV 1	18.4	67.0	413.0	3.15
NOV 8	19.0	137.0	479.0	2.9
NOV 22	21.0	105.0	577.0	2.75
NOV 29	22.5	182.0	514.0	2.95
DEC 6	30.7	222.0	618.0	2.9
DEC 20	22.6	172.0	504.0	2.9

1970 AUGER HOLE 5 DATA

JAN 3	25.3	160.0	457.0	2.9
JAN 17	26.8	195.0	493.0	2.8
JAN 24	26.0	157.0	485.0	2.9
JAN 31	28.4	130.0	442.0	2.85
FEB 7	28.4	155.0	483.0	2.8
FEB 14	40.0	172.0	296.0	2.75
FEB 21	32.7	220.0	572.0	2.65
FEB 28	48.3	187.0	526.0	2.79
MAR 7	34.0	267.0	662.0	2.73
MAR 14	35.0	232.0	586.0	2.85
MAR 21	35.0	362.0	816.0	2.7
APR 4	39.0	302.0	689.0	2.70
APR 11	43.0	255.0	628.0	2.75
APR 18	40.0	195.0	512.0	2.95
APR 25	532.0	1050.0	0.0	2.65
MAY 30	62.0	275.0	610.0	2.7
JUNE 6	59.0	265.0	582.0	2.75
JUNE 13	42.0	147.0	471.0	2.90
JUNE 20	33.0	162.0	531.0	2.95
JULY 1	30.0	185.0	508.0	3.0
JULY 17	29.0	191.0	506.0	2.75
AUG 6	32.0	225.0	525.0	2.85
SEPT 10	27.5	265.0	565.0	2.95
SEPT 16	25.0	220.0	541.0	2.82
SEPT 29	27.0	220.0	518.0	2.95

Table XIV

1969 AUGER HOLE 6 DATA

DATE	FLOW, GPD	ACID, PPM	SO4, PPM	PH
AUG 4	133.0	1.0	438.0	5.70
AUG 8	99.4	37.0	577.0	3.80
AUG 15	101.5	70.0	633.0	3.30
AUG 27	97.2	100.0	781.0	3.20
SEPT 3	82.5	102.0	685.0	3.2
SEPT 17	68.0	132.0	796.0	3.0
SEPT 25	63.0	5.0	401.0	6.1
OCT 4	60.1	57.0	576.0	3.6
OCT 18	61.0	42.0	437.0	4.5
OCT 25	56.7	7.0	352.0	6.05
NOV 1	54.3	10.0	412.0	5.2
NOV 22	61.0	82.0	646.0	3.3
NOV 29	66.5	45.0	515.0	4.3
DEC 6	65.7	66.0	363.0	6.1
DEC 20	60.0	132.0	669.0	3.05

1970 AUGER HOLE 6 DATA

JAN 3	78.0	115.0	661.0	3.1
JAN 24	83.0	355.0	1116.0	2.75
JAN 31	91.0	120.0	626.0	3.0
FEB 7	103.0	515.0	1400.0	2.5
FEB 14	205.0	900.0	1570.0	2.5
FEB 21	247.0	490.0	1074.0	2.5
FEB 28	191.0	357.0	967.0	2.65
MAR 7	238.0	530.0	1130.0	2.65
MAR 14	335.0	520.0	1127.0	2.75
MAR 21	370.0	537.0	1085.0	2.65
MAR 28	450.0	480.0	984.0	2.6
APR 4	450.0	475.0	949.0	2.9
APR 11	312.0	415.0	860.0	2.65
APR 18	312.0	225.0	563.0	2.95
MAY 30	450.0	325.0	644.0	2.8
JUNE 6	425.0	330.0	676.0	2.65
JUNE 13	362.0	167.0	620.0	2.75
JUNE 20	277.0	338.0	736.0	2.8
JUNE 26	229.0	241.0	630.0	2.9
JULY 1	197.0	272.0	650.0	2.85
JULY 7	165.0	300.0	720.0	2.7
JULY 17	141.0	306.0	745.0	3.7
AUG 6	200.0	347.0	757.0	2.8
AUG 19	102.0	647.0	1229.0	2.6
AUG 26	304.0	405.0	783.0	2.8
SEPT 10	134.0	392.0	810.0	2.9
SEPT 16	114.0	267.0	720.0	2.75
SEPT 29	105.0	235.0	655.0	2.90

BIBLIOGRAPHIC: The Ohio State University Research Foundation
Pilot Scale Study of Acid Mine Drainage
Publication No. 14010 EXA

ACCESSION NO:

KEY WORDS:

Mine Drainage
Pyrite
Sulfides
Coal
Pollution Abatement
Industrial Waste
Ohio
Auger Holes
Underground Mines

A research facility has been developed to study pyrite oxidation and resulting acid mine drainage on a pilot scale basis. The test units include a small, long-abandoned drift mine (McDaniels mine) and six 33 inch diameter auger holes drilled in order to have comparable, isolated, experimental "mines." All units are in the Middle Kittanning coal seam in southeastern Ohio. The effect of oxygen concentration on acid production has been studied in the McDaniels mine. Experimental data and observations have shown the location of major reaction zones and indicated that bacterial catalysis of pyrite oxidation is not a significant factor in production of acid mine drainage. The auger holes are being monitored to determine the degree of similarity between holes. When the correspondence

BIBLIOGRAPHIC: The Ohio State University Research Foundation
Pilot Scale Study of Acid Mine Drainage
Publication No. 14010 EXA

ACCESSION NO:

KEY WORDS:

Mine Drainage
Pyrite
Sulfides
Coal
Pollution Abatement
Industrial Waste
Ohio
Auger Holes
Underground Mines

A research facility has been developed to study pyrite oxidation and resulting acid mine drainage on a pilot scale basis. The test units include a small, long-abandoned drift mine (McDaniels mine) and six 33 inch diameter auger holes drilled in order to have comparable, isolated, experimental "mines." All units are in the Middle Kittanning coal seam in southeastern Ohio. The effect of oxygen concentration on acid production has been studied in the McDaniels mine. Experimental data and observations have shown the location of major reaction zones and indicated that bacterial catalysis of pyrite oxidation is not a significant factor in production of acid mine drainage. The auger holes are being monitored to determine the degree of similarity between holes. When the correspondence

BIBLIOGRAPHIC: The Ohio State University Research Foundation
Pilot Scale Study of Acid Mine Drainage
Publication No. 14010 EXA

ACCESSION NO:

KEY WORDS:

Mine Drainage
Pyrite
Sulfides
Coal
Pollution Abatement
Industrial Waste
Ohio
Auger Holes
Underground Mines

A research facility has been developed to study pyrite oxidation and resulting acid mine drainage on a pilot scale basis. The test units include a small, long-abandoned drift mine (McDaniels mine) and six 33 inch diameter auger holes drilled in order to have comparable, isolated, experimental "mines." All units are in the Middle Kittanning coal seam in southeastern Ohio. The effect of oxygen concentration on acid production has been studied in the McDaniels mine. Experimental data and observations have shown the location of major reaction zones and indicated that bacterial catalysis of pyrite oxidation is not a significant factor in production of acid mine drainage. The auger holes are being monitored to determine the degree of similarity between holes. When the correspondence

between holes has been established, one hole will be used as a reference mine so that fluctuations due to hydrologic variations can be separated from effects of experimentally imposed changes in the other holes.

between holes has been established, one hole will be used as a reference mine so that fluctuations due to hydrologic variations can be separated from effects of experimentally imposed changes in the other holes.

between holes has been established, one hole will be used as a reference mine so that fluctuations due to hydrologic variations can be separated from effects of experimentally imposed changes in the other holes.

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W	05B	

5 Organization

Water Quality Office, Environmental Protection Agency

6 Title

Pilot Scale Study of Acid Mine Drainage

10 Author(s)

Ohio State University
Research Foundation

16 Project Designation

Water Quality Office, EPA 14010 EXA

21 Note

22 Citation Water Pollution Control Research Series, 14010 EXA 03/71
Environmental Protection Agency, Water Quality Office
Washington, D. C., March 1971

23 Descriptors (Starred First)

Mine Drainage,* Pyrite,* Sulfides,* Coal*
Pollution Abatement, Industrial Waste

25 Identifiers (Starred First)

Ohio,* Auger Holes,* Underground Mines*

27 Abstract

A research facility has been developed to study pyrite oxidation and resulting acid mine drainage on a pilot scale basis. The test units include a small, long-abandoned drift mine (McDaniels mine) and six 33 inch diameter auger holes drilled in order to have comparable, isolated, experimental "mines." All units are in the Middle Kittanning coal seam in southeastern Ohio. The effect of oxygen concentration on acid production has been studied in the McDaniels mine. Experimental data and observations have shown the location of major reaction zones and indicated that bacterial catalysis of pyrite oxidation is not a significant factor in production of acid mine drainage. The auger holes are being monitored to determine the degree of similarity between holes. When the correspondence between holes has been established, one hole will be used as a reference mine so that fluctuations due to hydrologic variations can be separated from effects of experimentally imposed changes in the other holes.

Abstractor E. E. Smith | Institution The Ohio State University

WR:102 (REV JULY 1969)
WRSIC

SEND, WITH COPY OF DOCUMENT, TO: WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

* GPO: 1970-389-930